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RELATIONSHIP OF TREATMENT METHODS TO SUSPENDED MATTER IN WATER

Harvey F. Ludwig, et al

Engineering Science, Incorporated

Prepared for:

Public Health Service

February 1964

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FINAL REPORT

Project Year 1963-1964

RELATIONSHIP OF TREATMENT METHODS TO SUSPENDED MATTER IN WATER

(Contract No. PH 86-63-84)

Prepared For

DIVISION OF WATER SUPPLY AND POLLUTION CONTROL

U. S. PUBLIC HEALTH SERVICE

By

ENGINEERING-SCIENCE, INC.

Head Office
150 East Foothill Boulevard
Arcadia, California

Research Center
4144 Telegraph Avenue
Oakland, California

February 1964

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HARVEY F. LUDWIG, PRESIDENT
RALF C. CARTER, MANAGER
WILLIAM D. BISHOP, PH.D., ASST. MANAGER
RICHARD E. WARNER, STAFF BIOLOGIST
JAN SCHERFIG, CHEMIST
WONSUK KIM, PH.D., RESEARCH ENGINEER

ENGINEERING-SCIENCE, INC.
RESEARCH AND DEVELOPMENT LABORATORY
4144 TELEGRAPH AVENUE
OAKLAND 9, CALIFORNIA
TEL: (415) 653-7454

27 March 1964

Mr. Ralph H. Holtje
Research and Training Grants Branch
Division of Water Supply and Pollution Control
Bureau of State Services
Public Health Service
Washington 25, D. C.

Dear Mr. Holtje:

This will transmit our final report pursuant to Contract No. 86-63-84, dated 10 February 1963, for research on the relationship of treatment methods to suspended matter in water. The work of this twelve-month period has been directed toward research in two areas: 1) development of methods for characterizing suspended matter in water supplies, and 2) determination of the effects of pH-controlled coagulation on different types of clay suspensions.

In the first area, investigations were carried out on methods of measuring the cation exchange capacity (CEC) of clay suspensions. A methylene blue method was developed and found useful because of the simple operations involved and the yielding of reproducible results. Possible applications of CEC data were explored.

In the second area, the control of pH in coagulation produced a significant effect on turbidity removal. The optimum pH of coagulation was shown to be dependent on the type and concentration of clay and the alkalinity of the water.

Further research in the matter of suspended matter and its relationship to treatment methods should consider such factors as: 1) the effectiveness of coagulant aids (e.g. bentonite, alkalinity), and 2) the testing of the practicality of the laboratory results of the present studies in pilot plant operations. Improvements in settling and filtration devices should be evaluated together.

Sincerely yours,

ENGINEERING-SCIENCE, INC.

Harvey F. Ludwig

Harvey F. Ludwig
President

Encl.

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FINAL REPORT

RELATIONSHIP OF TREATMENT METHODS TO SUSPENDED MATTER IN WATER

Contract PH 86-64-69 -- 10 February 1963 to 9 February 1964

by

ENGINEERING-SCIENCE, INC.
Harvey F. Ludwig, Project Director
Wonsuk Kim, Project Engineer
William D. Bishop, Project Engineer

ABSTRACT

Kaolinitic suspensions are generally difficult to coagulate by mere addition of alum. By control of pH, optimum coagulation conditions can be achieved in which increase of floc size and decrease of alum dosage result.

For low-concentration kaolinitic suspensions (<50 mg/l), the pH to be attained is the isoelectric pH (pH_i) of the aluminum-hydroxo complex. This pH_i was found to be dependent on the suspension alkalinity. The relationship between pH_i and bicarbonate alkalinity was established.

With bentonitic suspensions and high-concentration kaolinitic suspensions, the optimum pH is less than the pH_i value for the suspension. These observations were explained.

A method of determining the type of clay in a suspension is proposed. A turbidity/CEC ratio can be used to differentiate approximately between bentonitic and kaolinitic clay suspensions.

A method for measuring the cation exchange capacity (CEC) of dilute clay suspensions was developed. The use of methylene blue dye provided a simple procedure and gave reproducible results.

In the case of bentonitic suspensions, alum dosage for coagulation may be predicted from the measurement of CEC and alkalinity, for a particular plant condition.

As yet, there is no sufficient basis for determining what chemical treatment should be used or what coagulant aids, such as bentonite, or amount of alkalinity should be added to a given suspension to produce the best flocculation at minimum cost. It is hoped that the results of our present study will shed light in this area -- on a pH-controlled coagulation, depending on the suspension alkalinity and the type of clay.

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I. INTRODUCTION

This final report summarizes research conducted during the period 10 February 1963 to 9 February 1964 by Engineering-Science, Inc. on the relationship of treatment methods to suspended matter in water.

GENERAL OBJECTIVES

The objectives of this research were to characterize suspended particulate matter in water, to conduct laboratory investigations involving a variety of water treatment processes, and to develop correlations and conclusions useful in engineering design and operation of water treatment processes in order to improve the removal of suspended matter.

SCOPE OF PRESENT STUDY AND RESULTS

In the characterization of suspended particulate matter in water, methods of determination of size distribution and cation exchange capacity (CEC) were studied.

Several procedures for determining particle size distribution and concentration were attempted but with little success. The difficulties involved were noted for possible future study.

For the determination of suspension CEC, a modified methylene blue method was developed and found promising in comparison to other conventional methods. The CEC of dilute clay suspensions could be measured without concentrating the suspended matter; the method was fairly simple and reproducible.

The use of measured CEC data in the coagulation process was investigated. It was found that the suspension CEC data could be used to predict alum dosage, depending on the alkalinity. However, this was applicable only to bentonitic suspensions and for a certain mixing condition. The ratio of turbidity/CEC was found indicative of the type of clay in the suspension. A later experiment showed that the type of clay was important in the selection of treatment method.

The present trend in practice toward better pre-treatment before filtration focused our attention on the optimization of coagulation conditions through pH control.

Particulate mobility measurements and jar tests were carried out in the study. Several modifications in the procedure for mobility measurement were made resulting in better reproducibility.

In the study of constant-pH coagulation, variables such as alkalinity, types of clays, concentrations of clays, etc. were considered. Two important results were obtained. First, it was found that the isoelectric pH of the aluminum-hydroxo complex depended on the suspension alkalinity; this relationship was established. Second, the optimum pH of coagulation was found to be the same as the isoelectric pH (pH_i) of the aluminum-hydroxo complex for low-concentration kaolinite suspensions, but not for bentonite and high-concentration kaolinite suspensions.

The significance of the results were evaluated, and the direction was set for further study in the improvement of water treatment processes.

PROJECT STAFF

Engineering-Science, Inc. staff for this study included Mr. Harvey F. Ludwig as project director, Dr. William D. Bishop, Project Engineer during the first quarter, and Dr. Wonsuk Kim Project Engineer during the latter three quarters.

Mr. Ralf C. Carter and Mr. Jan W. Scherfig made valuable suggestions in the course of the study.

ACKNOWLEDGEMENTS

The counseling given by Professor Warren J. Kaufman of the University of California, Berkeley, is greatly appreciated. The suggestions of Mr. James E. Cripps of the California State Department of Public Health, with regard to the development of the methylene blue method, were valuable contributions in the investigations.

II. PARTICLE SIZE DISTRIBUTION

Initially, investigations were directed toward procedures for determining the size distribution and concentration of particulate suspended matter in water.

For the measurement of particle size distribution, fractionation of particulates into several size ranges between 0.1 μ and 5.0 μ was attempted. A microscopic method was used for determining the number of species (e.g., organic, inorganic, plankton) of suspended matter in fractionated and unfractionated samples. Other methods for the determination of size distribution were evaluated for their applicability to measurements on dilute suspensions.

SIZE FRACTIONATION

Two methods of size fractionation were tested. First, the use of Millipore Filters of different pore sizes permitted the concentration of suspended matter in a given suspension. However, the fractionation of particles into size ranges, in the manner of a series of sieves, was not successful due to pore clogging by small particles. This clogging resulted in the retention of particles smaller than the designated pore sizes, giving erroneous fractionation. The use of "Calgon" to enhance the state of dispersion did not prevent clogging.

Second, the more conventional gravity separation method was investigated. It was possible to separate each size fraction of particles by repeated settling in a quiescent state. However, this method was time consuming, and a large volume of suspension had to be processed in order to obtain a significant weight of particles in each size range. In addition, the uncertainty of particle densities, which vary according to the kind of suspended matter, limited the use of the gravity method. The use of centrifugation for the separation also suffered the same drawbacks.

MICROSCOPIC METHOD

In the study of microstraining conducted by Carter and Ludwig (1), a microscopic method was used for identifying the kind and size of suspended matter and for determining size distribution in the range of 2 to 100 μ.

In the present study, suspended matter was collected on a Millipore Filter and examined under a microscope. This direct optical measurement allowed identification of particles of fairly large sizes (2 to 100 μ). However, the method was very slow, and any particle smaller than 0.5 μ could hardly be observed and counted. In the succeeding experiment (coagulation tests), we came to a conclusion that particles of sub-micro size were more important in the process of coagulation, than the larger particles.

OTHER APPARATUS

There are several proprietary automatic particle counting devices; Lewis (2) has given the most comprehensive description of the apparatus available. The instruments and procedures can be classified into four main groups:

1. Oscillation Microscope Scanner
2. Light Spot Scanner
3. Electrolytic Conductance Pulse Counter
4. Scattered Light Particle Counter

For purposes of the present study, these instruments were not suitably adapted to dilute clay suspensions due to one or more of the following reasons:

1. The instrument was limited in the smallest size particle measurable -- usually about one micron.
2. In the case of photoelectric devices, the resolution was not sufficient when dealing with relatively dense clay suspensions.
3. Some of the procedures required the addition of a certain chemical for purposes of measurement. This introduced a variable with regard to changes in the surface characteristics of the suspended matter, and, consequently, changes in the state of dispersion.
4. The calculations involved in reducing the data were time consuming.
5. The method assumed uniformity in the properties of the suspended matter in terms of refractive index and dielectric constant; such uniformity may not hold for a suspension in raw water.
6. The apparatus was expensive.

On the whole, the characterization of suspended particles, in terms of number of particles per unit volume, size distribution, and the kind of suspended matter, is almost impossible with presently available equipment for fast, dependable, and economical measurement.

Turbidity in raw water is due to the presence of particles of sizes greater than the shortest wave-length of visible light (i. e., 400 mμ). But the important size fraction in the coagulation process is the sub-microscopic, due to the greater susceptibility to chemical reaction and Brownian movement. These sub-microscopic particles cannot be measured by the use of visible light.

However, some light can be thrown on the character of suspended matter, including sub-microscopic particles, by another method: the measurement of cation exchange capacity (CEC).

III. MEASUREMENT OF CATION EXCHANGE CAPACITY

DIFFICULTIES IN THE CONVENTIONAL METHODS

The importance of the cation exchange capacity (CEC) of clay in the coagulation process was shown in early studies by Langelier and Ludwig (3). The measurement of suspension CEC was judged necessary for understanding the coagulation phenomena in the present studies.

The methods of CEC measurement used on soil samples are very well established. Seemingly applicable soils methods for dilute suspensions were selected for our study. They were a versenate method (4), a conductivity method (5), and a method employing a cation exchange resin. The above three methods were tested on a dilute clay suspension, but without success. These and other conventional methods of CEC measurement could not be used on dilute clay suspensions due to the following reasons:

1. The conventional methods required concentrations of clay or soil in the samples of at least 50 mg, as dry or concentrated slurry, for reliable results. For concentrating suspended matter from a dilute suspension (<100 mg/l), the Millipore Filter and high speed centrifuge were considered. In the case of the Millipore Filter, clogging of the pores prevented collection of a significant weight of solid. In addition, the transfer of collected sample from the filter involved error. In the case of centrifugation Packam (6) showed that a large volume of liquid suspension must be centrifuged to collect a sufficient quantity of suspended matter. According to Michaels and Morelos (7), the centrifuge method cannot collect fine colloidal particles in the alkaline pH range (pH > 7.0).

2. Most of the conventional methods of CEC measurement employ a method for saturating <u>all</u> exchangeable sites with Na^+ or NH_3^+ ions followed by measurement of these ions. Therefore, the CEC determined by these methods represents <u>total</u> exchangeable sites; whereas, in natural clay suspensions, some exchangeable sites are already occupied by tightly-held cations (divalent), and these cations may not be replaced by cations added as coagulants in the process of coagulation. Therefore, the CEC determined by conventional methods may not represent the actual in-situ CEC of the natural suspension. In the present investigations the latter is of interest with regard to the coatulation process.

Hence, some other method had to be found for overcoming the above two drawbacks in the conventional methods.

METHYLENE BLUE METHOD

In 1950, Robertson and Ward (8) proposed the use of methylene blue (MB^+) dye for measuring the CEC of clay. Their results indicated that a fair agreement existed between CEC measured by Ba^{++} and CEC measured by MB^+. Since they used this method on dry samples, a modification had to be made for dilute clay suspensions. This modified method enabled us to measure the CEC of dilute suspensions with a relatively simple laboratory operation and required only five minutes to make a single determination.

Methylene Blue (MB^+) is a cationic organic dye which does not hydrolyze in the manner of Al^{+++} or Fe^{+++}. Jenny (9) indicated that MB^+ is more strongly cationic than any inorganic cation. MB^+ is a chloride salt with three benzene rings and with a molecular weight of 319.9.

Procedure

The procedure used in the CEC measurement was as follows: To 100 ml of clay suspension, appropriate volumes of one mg/ml MB^+ were added and mixed well; in order to separate the suspended matter from the medium, the mixture was filtered through a 0.45 μ Millipore Filter. The first 50 ml were wasted (reason explained below); the next 25 ml were collected, and the optical density was measured by a Bausch and Lomb spectrophotometer (2 cm cell) at a proper wave length (see below). Optical density was converted to MB^+ concentration using a calibration chart. The difference between initial and filtrate dye concentration was taken as representing the micro-equivalents of MB^+ adsorbed per liter.

In this process, coagulation of clay particles was observed. This coagulation by cationic MB^+ agglomerated the submicro-size particles of clay, and the 0.45 μ Millipore Filter was able to remove particulates of all size ranges, therefore fulfilling the requirement that no suspended particulates be in the filtrate.

Factors Affecting the Results of the Methylene Blue Method

To obtain reproducible results, the following factors were evaluated in the measurement:

1. Wave length of spectrophotometer.

   MB^+ concentration could be determined by the optical method, but for any given wave length the concentration range which followed Beer's law of linearity was not very wide. Therefore, even though the maximum light absorption occurred at 670 mμ, several wave lengths were used to cover the wide range of dye concentrations involved.

This enabled us to measure a dye concentration without dilution. By using wave lengths of 400, 450, 500, 550, 600, and 640 mμ, we could detect dye concentrations in the range of 0.3 mg/l - 70 mg/l.

2. Dye adsorption by Millipore Filter (Figure 1).

The amount of dye adsorbed by the filter depended on the concentration of dye solution, but near-saturation of the filter was reached after filtering 75 ml of solution regardless of dye concentration. When the filter was pre-treated by soaking in 100 mg/l dye and washed with distilled water, saturation was reached after filtering 50 ml of the test clay suspension with dye.

3. Initial dye concentration and MB^+ adsorption on clays (Figure 2).

MB^+ adsorption increased with the increase of initial dye concentration up to a certain value of dye concentration after which the MB^+ adsorption was constant. As shown in Figure 2, the saturation value of MB^+ (or CEC) could be observed when initial dye concentration was greater than ~150 percent of suspension CEC or when the final dye concentration (filtrate) was more than one-third of the initial dye concentration. This concentration could be determined when the dye concentration in the filtrate and the initial dye concentration were compared. To guarantee being above this initial concentration, two or three tests should be run for a given suspension. However, adding too great an excess of dye in order to provide a concentration above ~150 percent of CEC is undesirable because the sensitivity of measurement suffers.

4. Concentration of clay (Figure 3).

When the concentration of clay was increased, MB^+ adsorption increased in the same ratio, and the linear regression line passed through the origin (i.e., no adsorption at zero clay concentration). This indicated that MB^+ adsorption was a function of the surface area of the suspended matter only and that the suspended solids concentration itself did not interfere in the accessibility of MB^+ to exchange sites due to high clay concentrations in the range shown in Figure 3.

5. Time of contact before filtration.

The adsorption of MB^+ was almost instataneous, and the CEC was the same whether the reaction time between MB^+ and clay was one minute, ten minutes, or one hour. Robertson and Ward (8) found that the sample must be shaken at least 20 minutes for a clay slurry, but we found that shaking was not necessary for dilute suspensions. This may be due to the easy accessibility of dye to exchange sites of clay in dilute suspension.

FIGURE 1

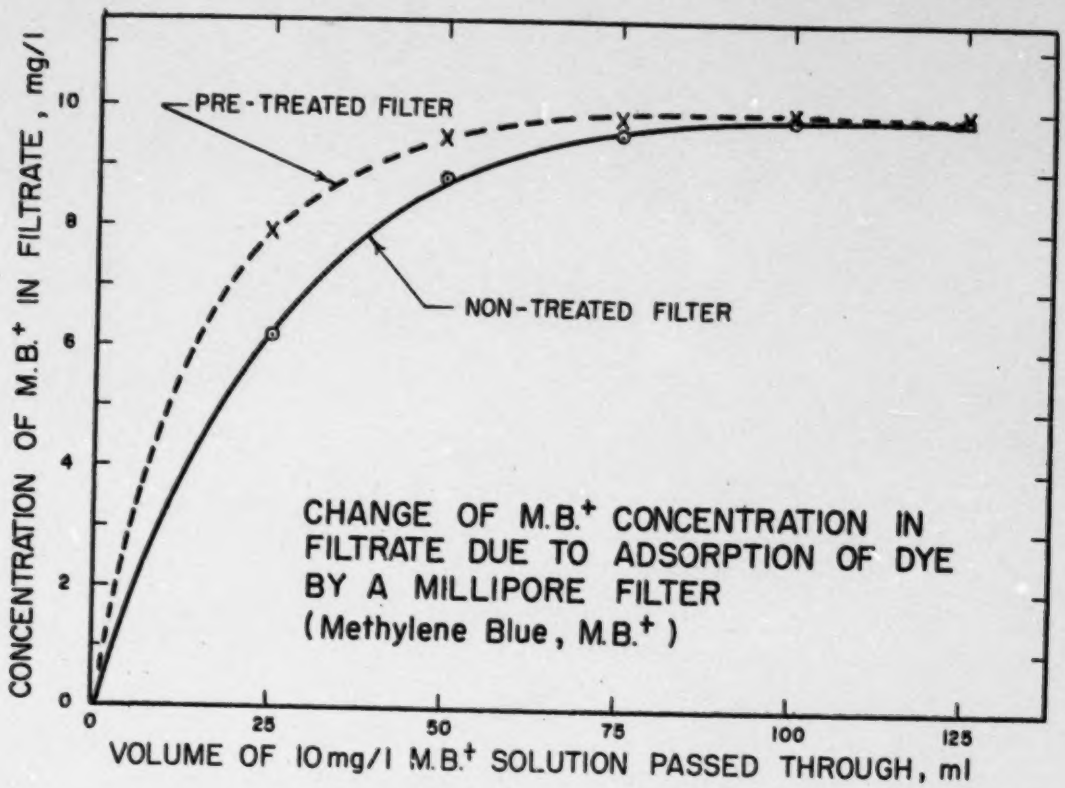


FIGURE 2

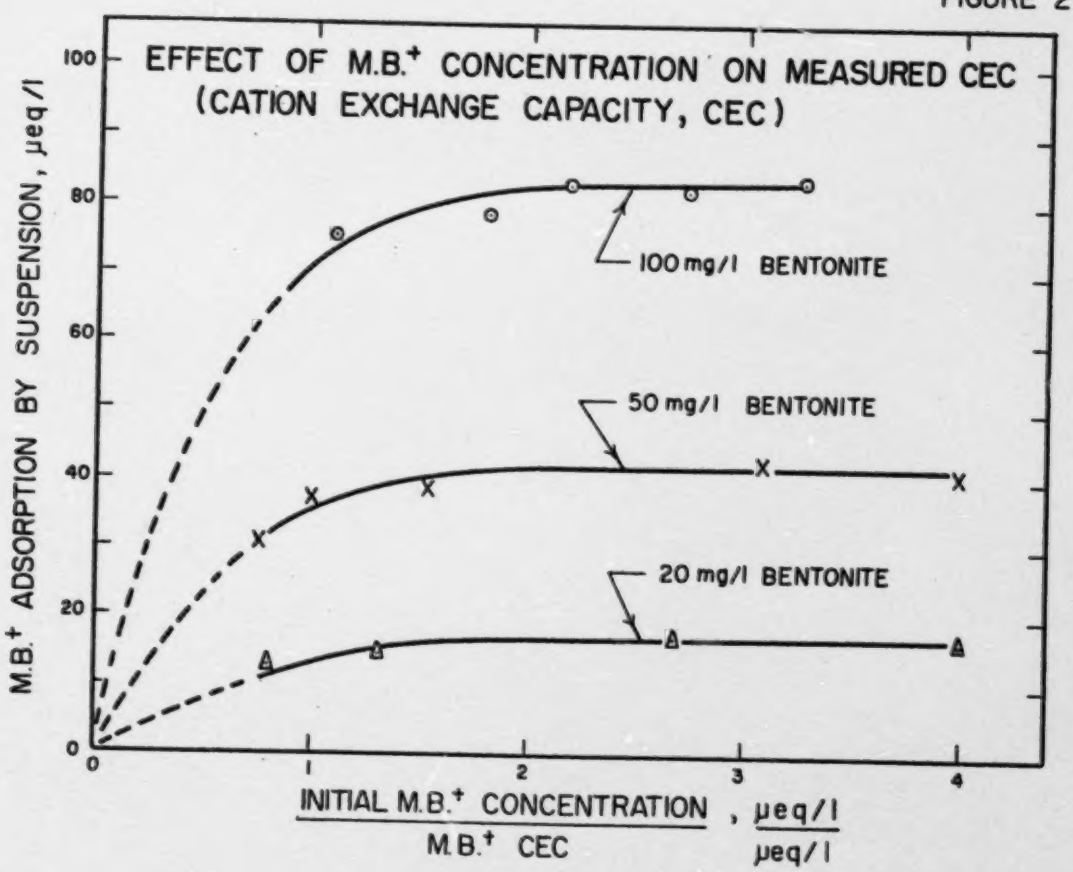


FIGURE 3

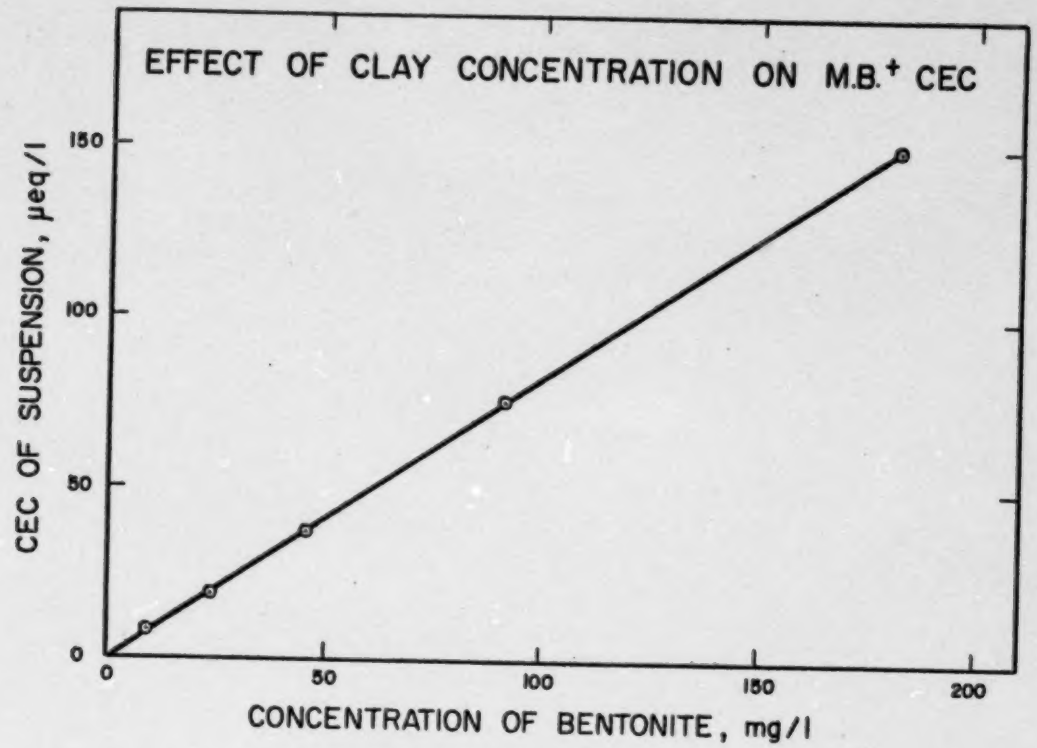
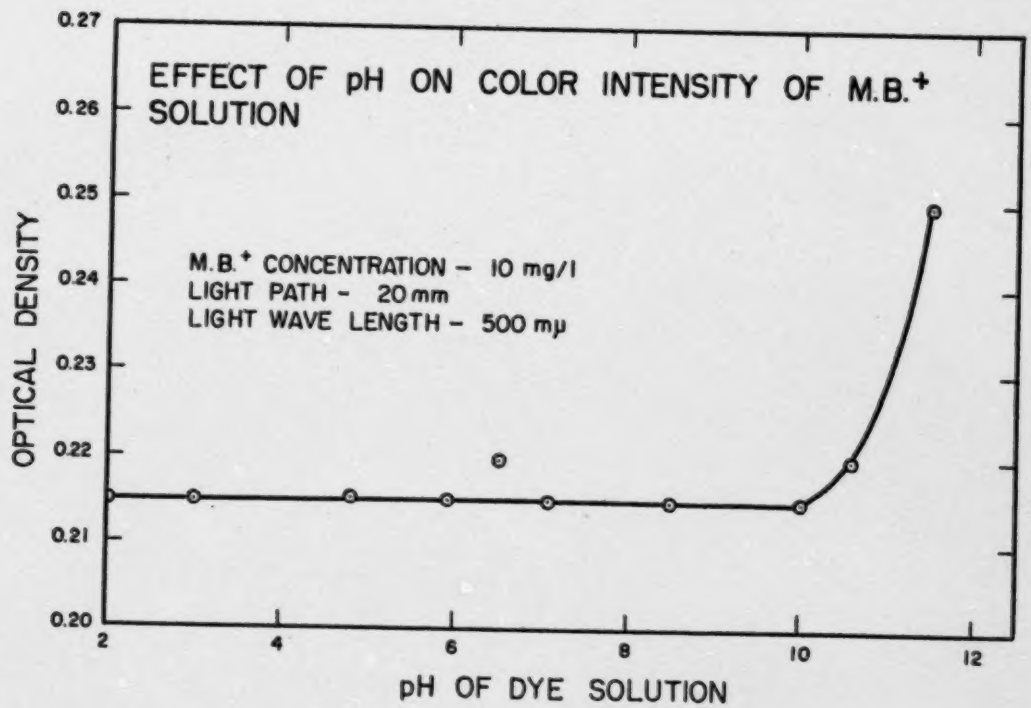


FIGURE 4



6. Change of color intensity of dye with pH.

Since clay suspensions may have a wide range of pH, it is essential for the dye indicator to have a stable color which does not change with pH. Figure 4 shows that MB^+ color intensity is constant at pH 2-10; this dye will serve the purpose satisfactorily in ordinary water.

7. Fading of MB^+ color with time.

Robertson and Ward (8) noted the necessity of preparing fresh MB^+ solutions once a week, because of the fading of color. When various concentrations of MB^+ were stored in a shaded area for one month during the present investigations, a slight decrease in color could be detected for an MB^+ solution at less than 6 mg/l concentration, but no change in color was observed above this concentration of MB^+. Hence, it is not necessary to prepare dye solution weekly. A small amount of chloroform should be added to the MB^+ to aid in preventing biological activity.

Comparison of CEC Results from the Methylene Blue and Conventional Methods

For checking the MB^+ method of CEC measurement against conventional methods, three kinds of clay were tested. Among the large number of conventional methods, the calcium method was recommended by Jackson (10), and this method was used for comparison. It was necessary to make the comparison test at slurry concentrations of clay because the conventional method cannot be used for dilute suspensions. After pre-treatment of clay with 1.0 N NaOAc, Na^+ was exchanged with either Ca^{++} or MB^+. In addition, the CEC of a non-pretreated dilute clay suspension (100 mg/l) was measured by MB^+. The results are shown in Table I.

TABLE I

CEC OF CLAYS BY Ca^{++} AND MB^+

Pre-treated with Na OAc	Exchanged Cation	Bentonite meq/100 gr	Illite meq/100 gr	Kaolinite meq/100 gr	Conc. of Clay
yes	Ca^{++} 1st test	88.0	24.9	9.4	10 gr/l
	Ca^{++} 2nd test	84.5	24.0	8.3	10
	Average	86.3	24.5	8.8	10
yes	MB^+ 1st test	105.0	27.8	9.5	10
	MB^+ 2nd test	108.0	27.8	9.5	10
	Average	106.5	27.8	9.5	10
no	MB^+ in dilute suspension	83.0	18.2	9.5	0.10

The results show that MB^+ CEC was generally 10 to 20 percent greater than Ca^{++} CEC. This may be due to the stronger cationic property of MB^+ compared to Ca^{++}. The lower value of CEC found in the dilute suspension compared to that of the clay slurries can be explained by the fact that the slurries of clay were pre-treated with 1.0 N Na OAc, and all the exchange sites were filled with Na^+ and then replaced by MB^+. But in the dilute suspension, cations such as Ca^{++} or Mg^{++} were not replaced by Na^+ because the clay particles were not subjected to high Na OAc concentration. The difficulty of replacing tightly-bound Ca^{++} and Mg^{++} in the dilute MB^+ concentration may have resulted in a low CEC value in the dilute suspension.

The minimum measurable concentration of MB^+ was ~ 0.3 mg/l, and this value corresponded to about 10 mg/l of kaolin suspension or one mg/l of bentonite suspension.

IV. APPLICATION OF CEC DATA

The coagulation theory of Langelier and Ludwig (3) holds that charge neutralization of particles by Al^{+++} (perikinetic reaction) is controlled by the CEC of the suspension, and that the aluminum hydroxide floc which binds the clay particles (orthokinetic reaction) is formed through the inter-action of alum and the suspension alkalinity. From this, therefore, it may be possible to predict alum demand, for a given suspension, by measuring the CEC and alkalinity when there is any firm relation among CEC, alkalinity, and alum dosage. Another use that was considered for CEC data was in the identification of the type of clay in a suspension. Generally, bentonite suspensions have higher CEC values and lower turbidities than kaolinite suspensions of the same weight concentration. The significance of the identification of the type of clay in a suspension will be discussed in the following chapters.

PREDICTION OF ALUM DOSAGE

For studying the relationship among CEC, alkalinity, and alum dosage, synthetic clay suspensions with different types and concentrations of clay and with various alkalinities were prepared for jar test coagulation.

Jar Test Procedure

Clay suspensions of 50 mg/l and 100 mg/l weight concentration of clay were prepared with distilled water. The clays tested were bentonite, illite, and kaolinite mixed in various proportions or taken alone. Alaklinity was set at 0.2, 0.4, 1.0, 2.0, and 4.0 meq/l with dosium bicarbonate.

The source of clays were as follows:

TABLE II

SOURCE OF CLAY SAMPLES

Clays	Source
Kaolinite	Baker and Adamson Co.
Illite	Illinois Clay Prod. Co.
Bentonite U.S.P.	Robinson Laboratory

Jar tests were made on 500 ml samples. After simultaneous addition of a series of alum dosages, the suspensions were mixed for 10 minutes with paddles

at 40 rpm and settled for 10 minutes. Optical densities of the supernatants were read on a B & L spectrophotometer at a wave length of 400 mμ and converted to turbidity using calibration charts. The CEC was determined by the previously-described method for each suspension, and the pH values of the supernatants were measured electrometrically.

Results of the Jar Tests

Residual turbidity vs. alum dosage curves were plotted from the jar test data, and the alum dosage corresponding to a turbidity decrease of 50 percent of initial was found (D_{50}). This particular percent reduction in turbidity (D_{50}) is located near the inflection point of the Turbidity-Alum Dosage curve and is convenient to use as an arbitrary value for comparison studies. This dosage (D_{50}) was chosen also because of fair reproducibility and because D_{50} dosage was fairly close to optimum alum dosage for maximum turbidity removal. Two types of correlations were investigated. No straight line relation or any other pattern of relations could be found between alkalinity and alum dosage for a suspension of fixed CEC. Figures 5 and 6 show the relationship between CEC and alum dosage (D_{50}) at different alkalinities. Linear relationships were found between CEC and alum dosage when the CEC was greater than 10 μeq/l.

Figures 5 and 6 indicated the following:

1. Good linear correlation between CEC and alum dosage could be found at 0.2, 0.4, 1.0, and 2.0 meq/l alkalinity. The correlation was poor at 4.0 meq/l alkalinity.

2. The slope of the linear regression line increased as alkalinity increased.

3. For the 1.0 and 2.0 meq/l alkalinity lines, the slope reversed at CEC values less than 10 μeq/l. This reversal will be discussed later in the report in the discussion of pH control.

4. No flocculation could be observed at low alkalinity (0.2 and 0.4 meq/l) when the CEC was less than 10 μeq/l.

Application

Through the determination of suspension CEC and alkalinity alum dosage for D_{50} may be predicted from Figures 5 and 6. However, the following drawbacks limit the use:

1. It was observed that the optimum alum dosage changed with the amount of energy input in the jar test mixing procedure.

FIGURE 5

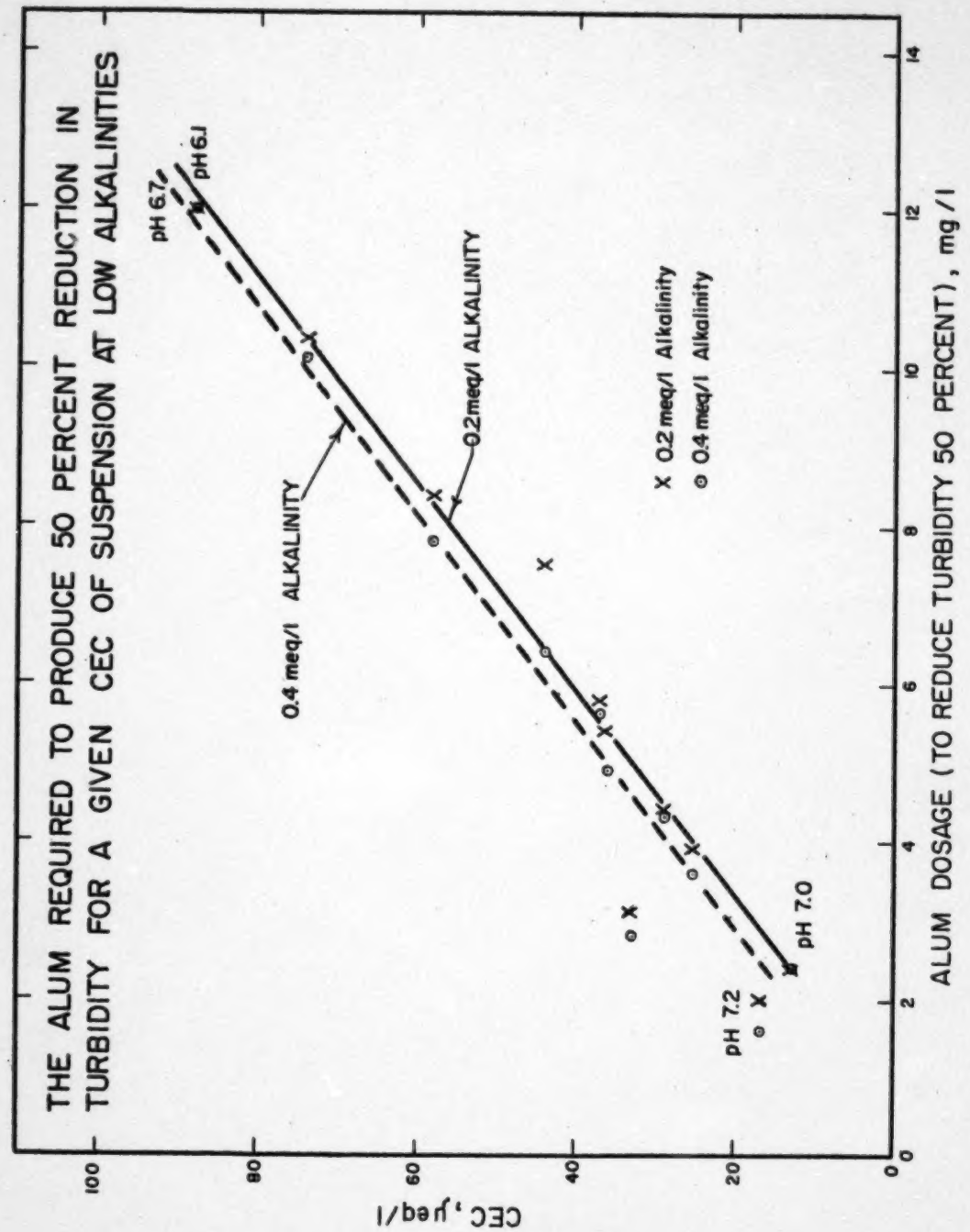
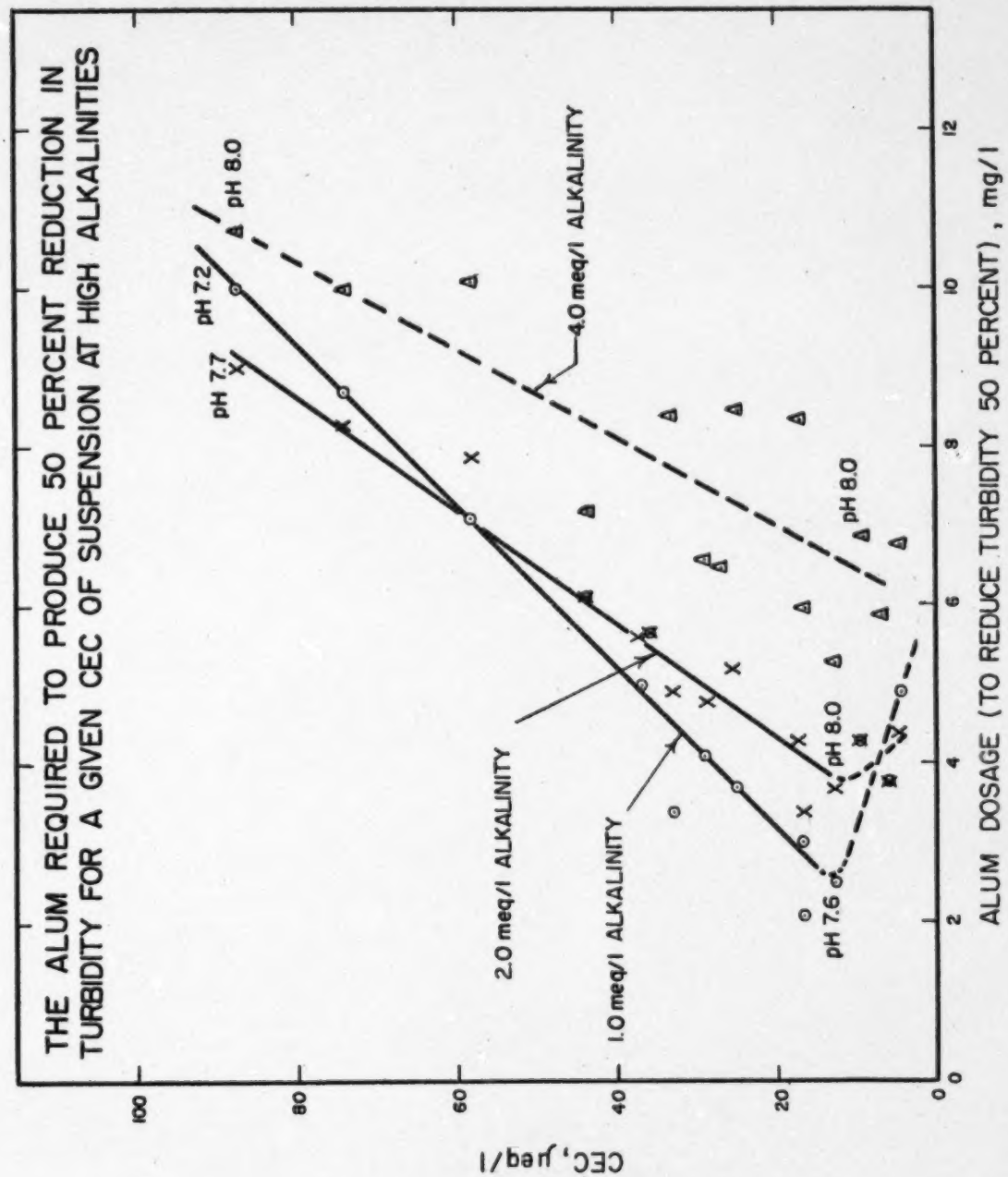

THE ALUM REQUIRED TO PRODUCE 50 PERCENT REDUCTION IN TURBIDITY FOR A GIVEN CEC OF SUSPENSION AT LOW ALKALINITIES
CEC, μeq/l
ALUM DOSAGE (TO REDUCE TURBIDITY 50 PERCENT), mg/l
0.4 meq/l ALKALINITY
0.2meq/l ALKALINITY
pH 6.7
pH 6.1
pH 7.0
pH 7.2
X 0.2 meq/l Alkalinity
⊙ 0.4 meq/l Alkalinity
0
20
40
60
80
100
2
4
6
8
10
12
14

FIGURE 6


THE ALUM REQUIRED TO PRODUCE 50 PERCENT REDUCTION IN TURBIDITY FOR A GIVEN CEC OF SUSPENSION AT HIGH ALKALINITIES
CEC, µeq/l
ALUM DOSAGE (TO REDUCE TURBIDITY 50 PERCENT), mg/l
4.0 meq/l ALKALINITY
2.0 meq/l ALKALINITY
1.0 meq/l ALKALINITY
pH 7.2
pH 7.7
pH 8.0
pH 8.0
pH 8.0
pH 7.6
0
20
40
60
80
100
2
4
6
8
10
12

2. The relationships in Figures 5 and 6 also may change in the presence of other dissolved ions.

3. No firm relationship was found for kaolinitic suspensions due to the fact that kaolinite has a very small CEC compared to bentonite; Figures 5 and 6 were based primarily on bentonite.

The approach described above can be applied in a plant only when mixing conditions and dissolved ions are taken into account by the ratio of D_{50} alum dosage (from graphs similar to Figures 5 and 6) and actual optimum dosage for the plant when the relationships have been established by test for each plant.

IDENTIFICATION OF THE TYPE OF CLAY

It is generally observed that bentonitic suspensions behave differently from kaolinitic suspensions in the coagulation process. When clays are divided roughly into two types for coagulation purposes, kaolinitic suspensions may include quartz, kaolinite, mica, and illite which are relatively large-sized particles having low CEC values; whereas, bentonitic suspensions include montmorillonite, beidellite, etc. consisting of relatively fine particle sizes and high CEC values. Rolfe (11) noted that median size of kaolinite is about 1.0 micron; whereas, the size of bentonite particle is less than 0.5 micron. This may mean a higher turbidity in the kaolinite suspension than in the bentonite suspension for the same weight concentration. This was shown to be the case in our experimental suspensions. The kaolinite showed a turbidity two and one half times greater than the bentonite at 50 mg/l clay concentration.

If the ratio of turbidity/CEC is designated as the degree of coarseness, the ratio may indicate the type of clay, independently of the clay concentration. Table III shows the examples.

TABLE III

DEGREE OF COARSENESS

Clay	Weight Conc. mg/l	Turbidity mg/l	CEC mg MB^+/l	Degree of Coarseness
Bentonite	50	25	14.0	1.8
Kaolinite	50	64	1.5	42.7

Through the calculation of the ratio, the proportion of bentonite and kaolinite in a suspension may be approximated. In the following experiment, it was found that the two types of clay suspensions should have different pH control for an optimum condition for coagulation. It was hoped that this ratio would aid in the selection of the final pH of coagulation.

V. MEASUREMENT OF MOBILITY

In order to study optimum conditions for coagulation, it was desired to have available a method for measurement of the zeta potential of particles. This was considered to be an important factor in colloidal phenomena. Black (12) introduced the use of a microscopic electrophoresis method for this purpose in water treatment. The use of particle mobility (mobility being almost proportional to zeta potential) was strongly recommended by Riddick (13) as being the best control method in coagulation. Several other investigators (6) (17) disagreed with this recommendation since the correlation of coagulation phenomena and clay mobility was generally poor.

Consequently, measurements of mobility were made in the present studies for purposes of clarifying the mechanism involved in pH-controlled coagulation as well as for aiding in the resolving of the above controversy.

ZINC ELECTRODE SYSTEM

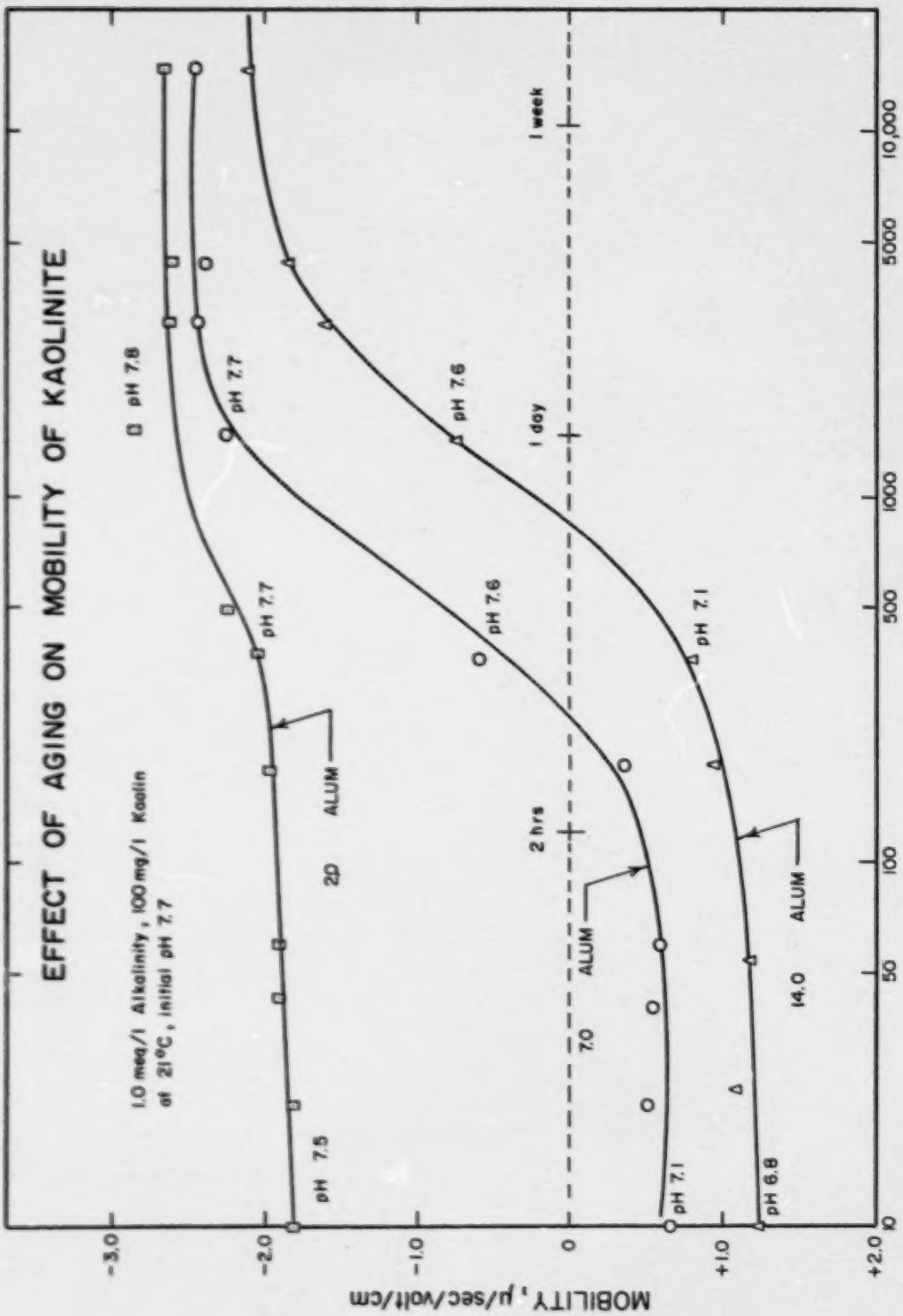
The apparatus used and the method followed were those developed by Black (12). The only modification made was in the electrode. Due to the difficulty and the necessity for the cleaning procedure using the $Hg - HgNO_3 - KNO_3$ electrode system, a new electrode system was investigated. It consisted of a $Zn - ZnSO_4 - Na_2SO_4$ system which was recommended by Glaser (14). When the new electrode system was checked with a mercury electrode system using a mobility standard of red blood cells (in phosphate buffer), the results were within 5 percent error of the standard mobility. The new electrode system did not require frequent cleaning, as was the case with the Black electrode. Mobility was measured at the upper and lower stationary levels and averaged. This averaging improved the reproducibility of the measurement.

EFFECT OF AGING ON THE MOBILITY OF CLAY PARTICLES

The mobility of clay samples was measured after a prescribed mixing and settling period. From our initial laboratory observations, it was found that any delay in measurement of mobility gave erroneous results. In determination of these deviations, a kaolin suspension (concentration 100 mg/l, alkalinity 1.0 meq/l) was coagulated with 2, 7, and 14 mg/l alum, without pH control, and the change of mobility with time was measured.

Figure 7 shows that mobilities of clay particles, as time passed, approached the original mobility (-2.7 μ/sec/volt/cm) of the suspension to which no alum was added. Figure 7 also indicates that the pH of the suspension increased with time.

FIGURE-7


EFFECT OF AGING ON MOBILITY OF KAOLINITE
1.0 meq/l Alkalinity, 100 mg/l Kaolin
at 21°C, initial pH 7.7
pH 7.8
pH 7.7
pH 7.6
pH 7.1
pH 7.7
pH 7.6
pH 7.5
pH 7.1
pH 6.8
20 ALUM
7.0 ALUM
14.0 ALUM
2 hrs
1 day
1 week
MOBILITY, μ/sec/volt/cm
-3.0
-2.0
-1.0
0
+1.0
+2.0
TIME AFTER ALUM ADDITION, MINUTES (LOG SCALE)
10
50
100
500
1000
5000
10,000

These results can be explained by introducing the equilibrium of the $CO_2 - HCO_3^- - CO_3^=$ system. When bicarbonate is a major component of the system, which was the case of the suspensions tested, the main dissociation is as follows:

$$2\ HCO_3^- \rightleftharpoons \overset{CO_2}{\underset{\uparrow\downarrow}{H_2CO_3}} + CO_3^=$$

When alum is added to a bicarbonate solution, H_2CO_3 is produced according to the following reaction, and supersaturation of H_2CO_3 (or CO_2) may occur temporarily:

$$Al_2(SO_4)_3 + 6\ NaHCO_3 + 6\ H_2O \longrightarrow 2\ Al(OH)_3\downarrow + 3\ Na_2SO_4 + 6\ \underline{H_2CO_3}$$

The maximum solubility of CO_2 at 20°C and one atmospheric pressure (with 0.03% CO_2 content in air) is 0.51 mg/l, and the pH at which 0.51 mg/l CO_2 (or H_2CO_3) in water comes to equilibrium with 1.0 millimol/l alkalinity is about 8.2. Hence, any pH lower than the equilibrium pH 8.2 (caused by alum addition) may approach 8.2 as time passes in attaining CO_2 equilibrium. (The resulting equilibrium pH will actually be less than pH 8.2 due to the reduction of total alkalinity by the escape of CO_2 into air.) This increase of pH may change the elctrical charge of the adsorbed aluminum-hydroxo complex, as Stumm (18) mentioned, and will lead to a charge reversal on the clay particles.

However, Figure 7 shows that this change of mobility is not significant within two hours after coagulation. Therefore, all the mobility measurements were made within this two-hour period.

VI. EXPERIMENTAL PROCEDURE FOR pH-CONTROLLED COAGULATION

NECESSITY FOR THE STUDY

There has been a great deal of work performed by various investigators on the effects of pH on coagulation. According to the studies of Theriault and Clark (15), Bartow and Peterson (16), Black and Rice (17), Stumm (18), and Packam (19), the pH of coagulation of turbid clay suspensions was found to be very important. However, the values reported for optimum pH of alum coagulation varied widely among these workers.

TABLE IV

OPTIMUM pH OF ALUM COAGULATION
(by Investigators)

Investigator	Optimum pH
Theriault and Clark (15)	5.5
Packam (19)	~ 7.0 (kaolinite)
Black (17)	7.6 - 7.8 (kaolinite)
Babbitt et al (20) (General)	< 7.0

An additional finding was introduced from our foregoing experiment, when it was observed that a good floc was formed at low alkalinity and high suspension CEC and also at high alkalinity and low suspension CEC, but the reasons were not clear.

Therefore, it was thought necessary to determine the optimum conditions for coagulation in terms of pH, alkalinity, CEC, and the type of clays, and to clarify the relationships among these factors.

PROCEDURE

In order to maintain constant pH in a series of jar tests, a known amount of sodium bicarbonate alkalinity was added to distilled water in the preparation of the synthetic suspension, and the initial pH was adjusted by adding HCl or NaOH. Next, alum and NaOH, in equivalent amounts, were added simultaneously. This method was the same as that used by Black (17). In this process, varying amounts of Na^+ were added in the form of $NaHCO_3$ and NaOH. The variation of Na^+ ranged from 0.4 to 2.0 meq/l. The effect of Na^+ in this range was investigated, and it was found that Na^+ had an insignificant effect on the turbidity removal and mobility of clay particles.

The order of addition of alum and the equivalent NaOH was investigated. A better turbidity removal could be achieved when alum and NaOH were added simultaneously or when NaOH was added first than the case when alum was added before the NaOH. In our experiment, alum and NaOH were added simultanously, as a standard practice.

The jar test procedure used was the same as the method used previously. To 500 ml of suspension, acid or alkali was added while being mixed, and alum and the equivalent NaOH were added simultanously. The time of mixing was measured from the time of alum addition. After being mixed for 10 minutes at 40 rpm, the suspensions were settled for 10 minutes, and the top 100 ml were decanted for optical density and pH measurements. In the jar test procedure, the use of rapid mixing (for one minute at 70 rpm in our test) ahead of slow mixing did not affect the turbidity removal;, therefore, rapid mixing ahead of slow mixing was not used, in order to simplify the procedure.

The mobilities of the samples were usually measured after the mixing and settling period. However, for a sample with good floc, the measurement was difficult due to floc settling in the electrophoresis cell. In order to overcome this difficulty, the suspension was mixed with alum for two minutes, and the mobility was measured immediately, before floc formation. In the case of bentonite even this step was not fast enough, and the floc had to be re-dispersed by physical stirring before measurement. The length of mixing time or degree of stirring did not affect the particle mobility. This was to be expected because chemical ion exchange is a fast reaction and should be independent of mechanical operation.

VII. RESULTS OF pH-CONTROLLED COAGULATION

EFFECT OF ALKALINITY ON COAGULATION

Effect of Alkalinity on the Optimum pH of Coagulation

The suspension investigated was kaolinite, at a concentration of 50 mg/l by weight.

The following observations were made based on the changes in turbidity that occurred for various final pH values of the suspensions as shown in Figure 8 for two of the six levels of alkalinity, at fixed alum dosage.

1. It was found that the optimum final pH of coagulation depended on the initial alkalinity present in the suspension. As the alkalinity was increased the optimum pH decreased, as shown in Table V.

TABLE V

OPTIMUM pH VALUES AT VARIOUS INITIAL ALKALINITIES

Initial Alkalinity, meq/l	0	0.4	1.0	2.0	4.0	6.0
Optimum final pH	8.3	8.0	7.6	7.3	6.9	6.6

Figure 8 shows the results of suspension of 0.4 and 2.0 meq/l alkalinity only.

2. The optimum pH of coagulation was found to be independent of alum dosage, but the pH range for good coagulation widened with the increase of alum dosage.

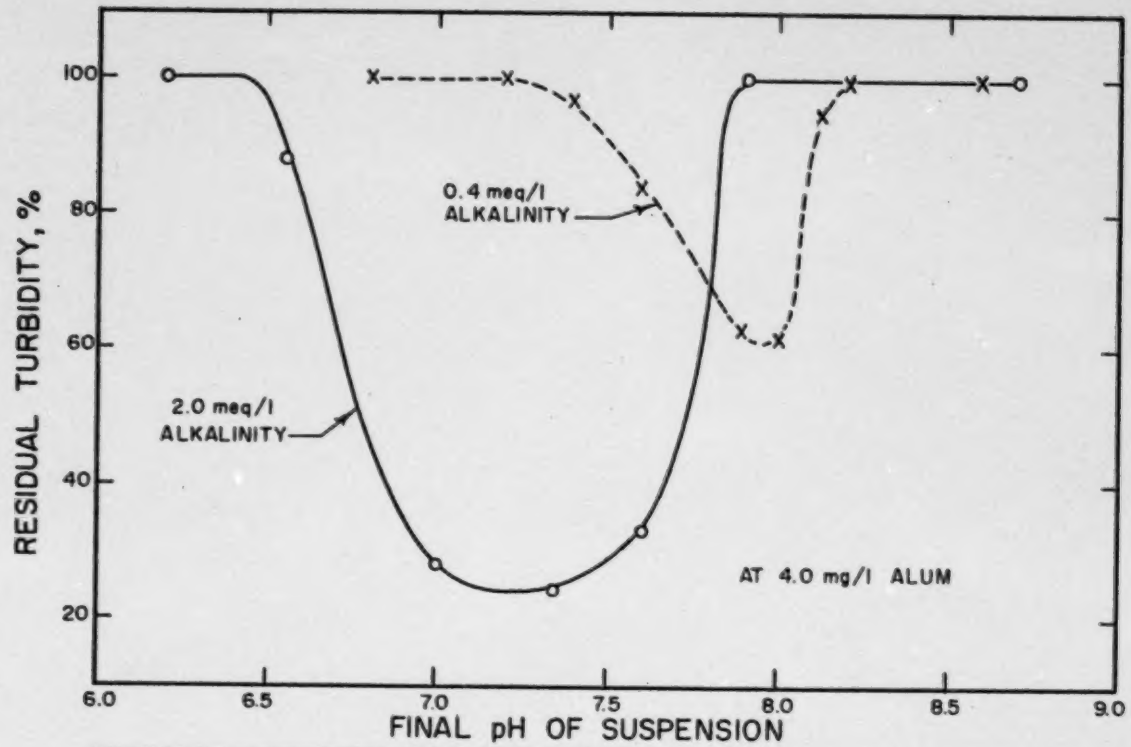
3. High alkalinity in the suspension gave better removal of turbidity than did low alkalinity, at the same alum dosage and at their respective optimum pH values.

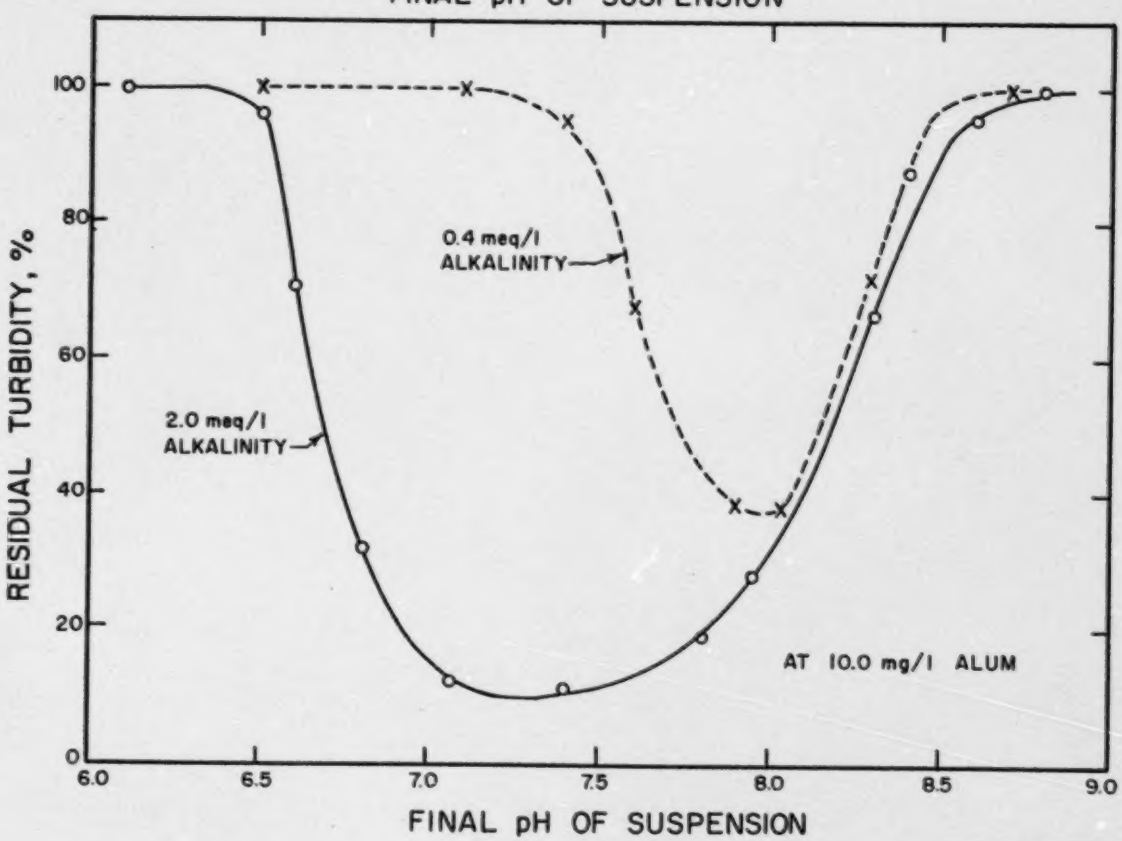
Coagulation Curves and Mobility of Kaolinite Suspensions

In order to determine the reason for the dip in the coagulation curves of Figure 8, more detailed study was made using kaolinite suspensions at 50 mg/l concentration and 1.0 meq/l alkalinity. Coagulation was performed at constant

FIGURE 8

EFFECT OF ALKALINITY ON THE OPTIMUM pH OF COAGULATION
(50 mg/l Kaolinite suspension)





pH values of 6.5, 7.5, and 8.5 and with various alum dosages. For this clay-alkalinity suspension, the optimum pH for coagulation was shown to be pH 7.6 (alkalnity 1.0 meq/1 -- see Table V).

The results shown in Figure 9 indicate:

1. The mobility of clay (kaolinite) became almost zero at pH 7.5 when the alum dose was high. It can be observed that at a pH near the optimum pH of coagulation, the mobility of clay approached zero at high alum dosage. A similar investigation was made on a 50 mg/1 kaolin suspension containing 0, 0.4, 2.0, 4.0 and 6.0 meq/1 bicarbonate alkalinity. The results are not shown here. The optimum pH of coagulation for each suspension also corresponded to the pH at which the clay charge became almost zero. This occurred for all cases when the alum dosage was more than 10 mg/1.

2. The zero clay mobility, induced by alum at pH 6.5, resulted in a poor coagulation shown in the upper curve of Figure 9. A good coagulation could be attained at pH 7.5.

3. The double flocculation also shown in the upper curve of Figure 9 noted by Kaufman (21), Langelier and Ludwig (3) was observable only at pH 6.5. No peptization (redispersion of floc) took place at pH 7.5 and 8.5, even at very high alum dosage.

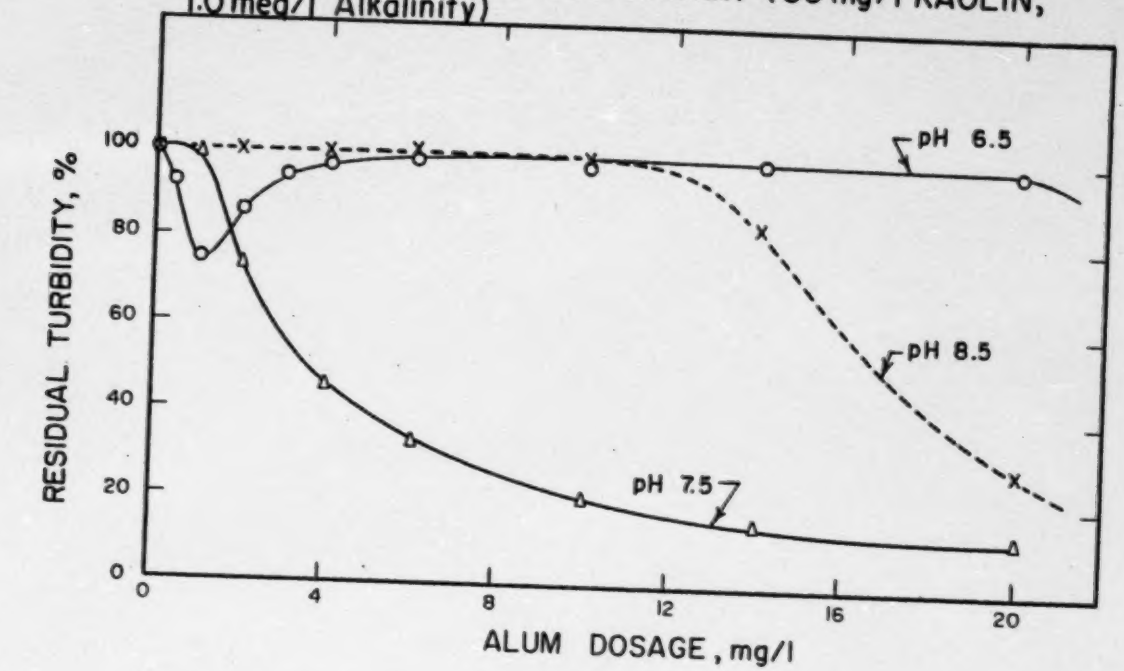
Relationship Between the Isoelectric pH of Aluminum Hydroxide and Suspension Alkalinity

In the foregoing results, the optimum pH, which was indicated by the dip of the pH-turbidity curves and by the mobility data, was taken as the isoelectric pH of $Al(OH)_3$ (the reason for this assumption is given in the following discussion) and plotted against the concentration of bicarbonate alkalinity. Since the initial bicarbonate alkalinity changed with the adjustment of pH discussed previously, the final bicarbonate concentration was calculated according to the method described by Olson, et al (22).

Figure 10 shows the dependence of pH_i on the initial and final bicarbonate concentration. There was a linear relationship between pH_i and final bicarbonate concentration when the HCO_3^- was greater than 1.0 meq/1. When the HCO_3^- concentration was less than 1.0 meq/1, hydroxide alkalinity had to be added in order to raise the pH to the value of the acutal pH_i, which may account for the non-linearity. When the linear regression line was extrapolated back to zero alkalinity it intercepted at $pH_i = 7.9$.

FIGURE - 9

EFFECT OF pH ON THE TURBIDITY REMOVAL AND MOBILITY OF KAOLIN SUSPENSION (50 mg/l KAOLIN, 1.0 meq/l Alkalinity)



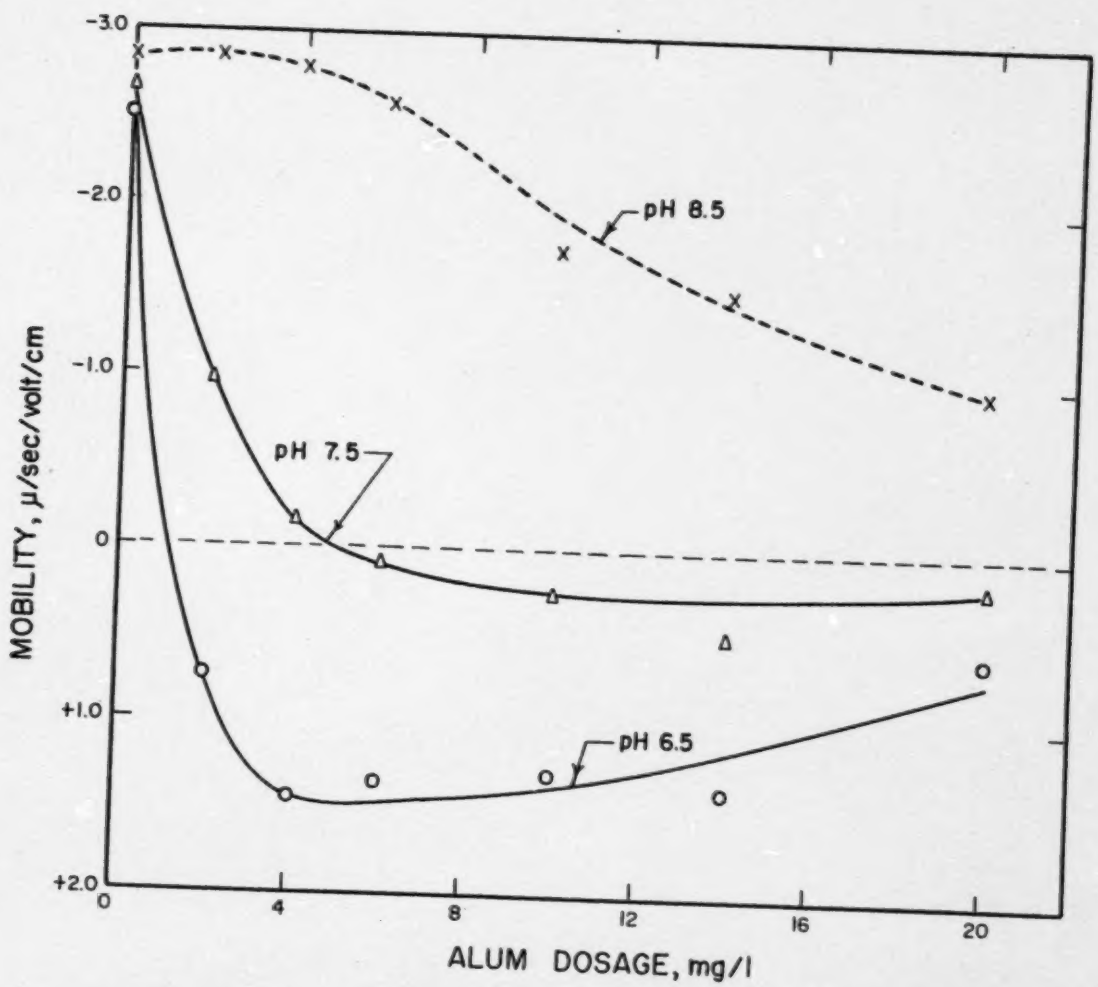
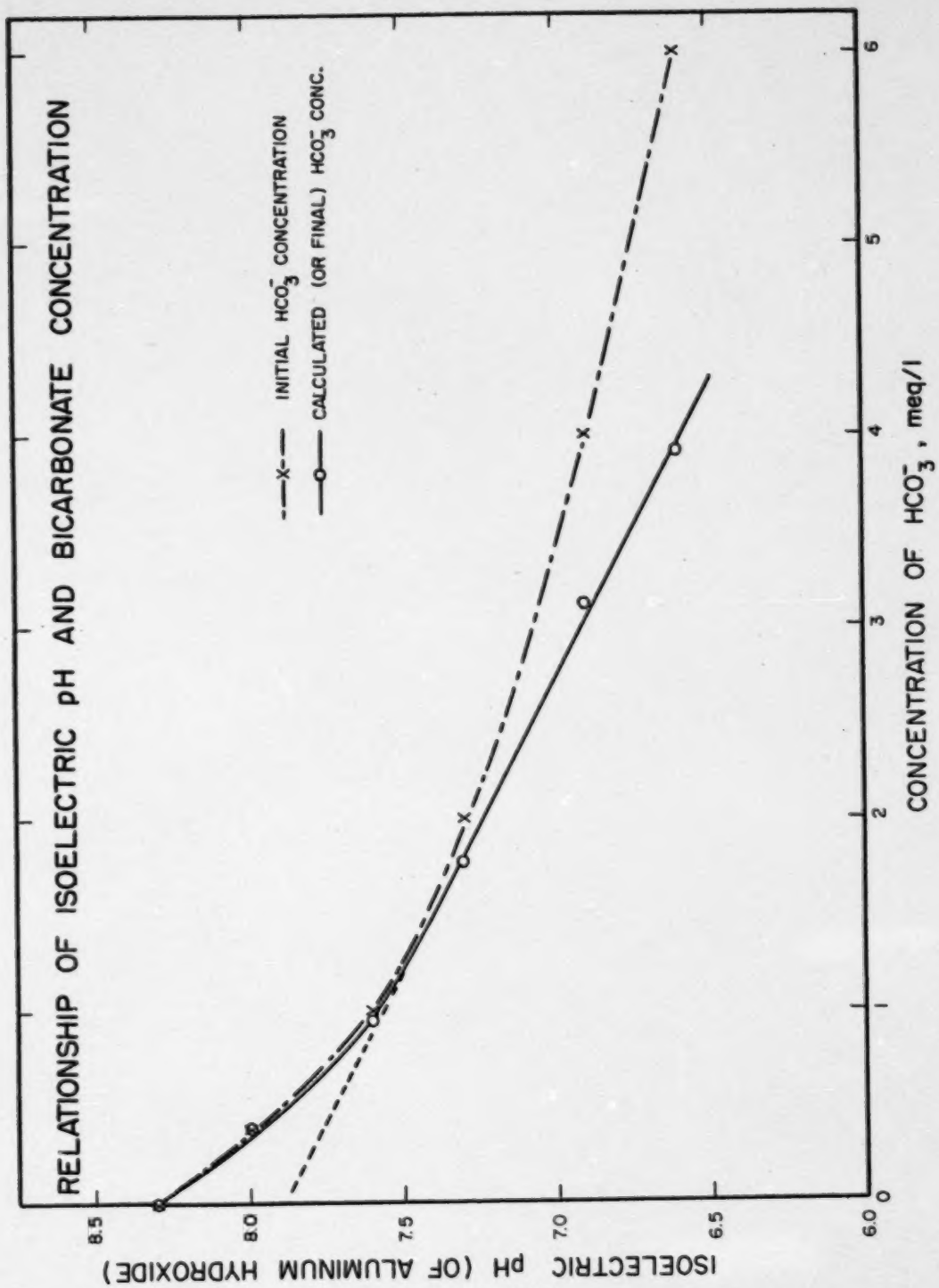


FIGURE - 10


RELATIONSHIP OF ISOELECTRIC pH AND BICARBONATE CONCENTRATION
INITIAL HCO_3^- CONCENTRATION
CALCULATED (OR FINAL) HCO_3^- CONC.
ISOELECTRIC pH (OF ALUMINUM HYDROXIDE)
8.5
8.0
7.5
7.0
6.5
6.0
CONCENTRATION OF HCO_3^-, meq/l
0
1
2
3
4
5
6

THE DIFFERENT BEHAVIORS OF BENTONITE AND KAOLINITE SUSPENSIONS IN COAGULATION

Thus far, only kaolinite suspensions were tested for the purpose of studying the pH effect. However, bentonitic suspensions are known to exhibit a very different response in the coagulation process. It was desirable to determine how pH-controlled coagulation affected the coagulation of bentonite and to compare the results with those of kaolinite.

Effect of the Type of Clay

Figure 11 shows the coagulation curves of pH vs. residual turbidity for two clays at constant alum dosage. Unlike the case involving kaolinite suspensions, bentonite suspensions did not show the minimum dip in the curve. Another difference was the increase in turbidity above the initial 100 percent shown by the low-alkalinity bentonite suspension. The turbidity increase was about 30 percent above the initial value; this was not observed in the case of the kaolinite suspensions.

Effect of pH

Figure 12 shows three turbidity-alum coagulation curves for constant pH values of 6.5, 7.5, and 8.5. For bentonite suspensions, the turbidity removal was most effective at pH 6.5, although the isoelectric pH of aluminum hydroxide was near pH 7.5 ($pH_1 = 7.6$) for this suspension of 1.0 meq/l alkalinity (see Figure 10). The alum dosage was the least, and the final turbidity was the least at pH 6.5 for the bentonite suspension.

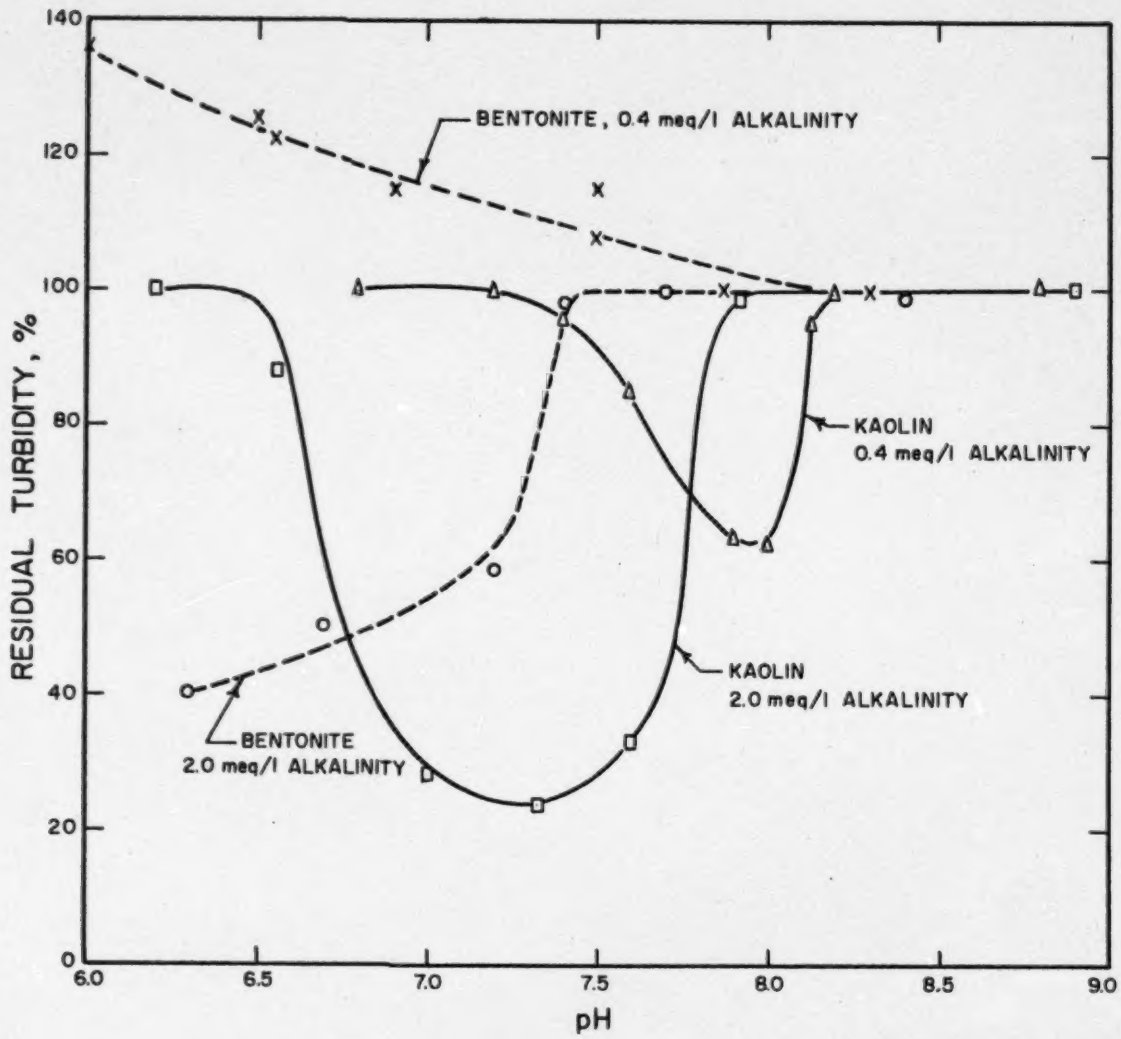
Study on the kaolinite suspensions showed that the best result could be obtained at pH 7.5, which was almost at the isoelectric pH of 7.6. At pH 6.5, flocculation was slight, and any further addition of alum resulted in peptization.

As was observed in Figure 11, Figure 12 also indicates an increase in turbidity for low dosages of alum for bentonite suspension only.

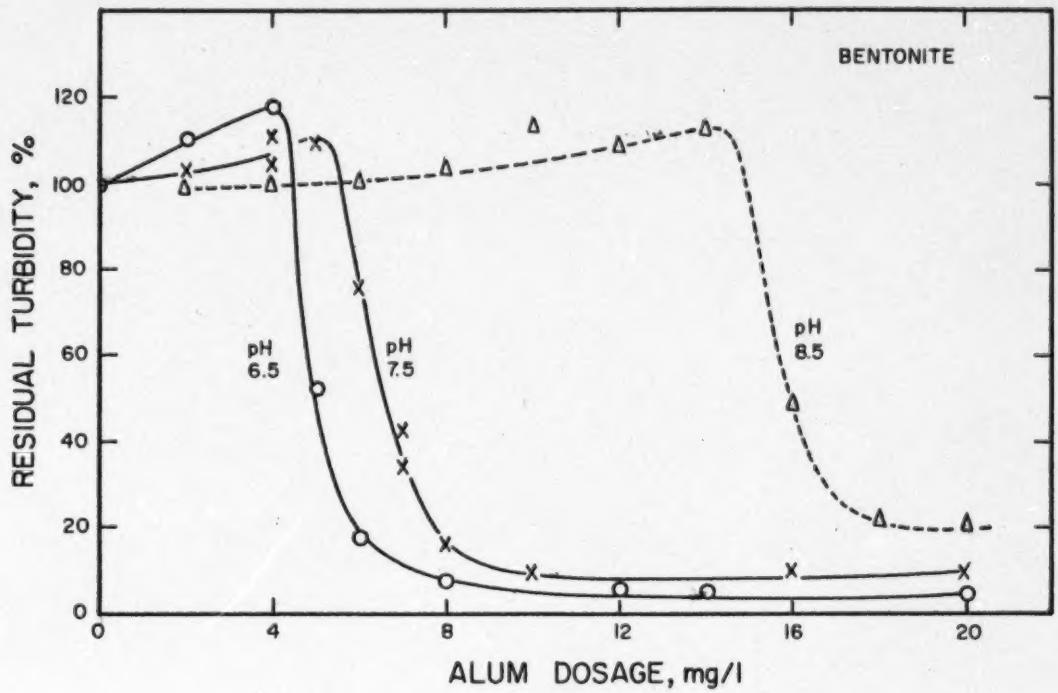
Effect of Alkalinity

Mobility and turbidity vs. alum dosage curves, at a constant pH of 7.5 and at three different suspension alkalinities are shown in Figures 13 and 14 for bentonite and kaolinite suspensions. Since the pH_1 of a suspension was found to be dependent on the alkalinity, the expected electric charge of the hydrolysis product of alum is indicated in Table VI for the three different alkalinities.

EFFECT OF THE TYPE OF CLAY ON THE pH-COAGULATION CURVE
(Clay, 50 mg/l by weight ; Alum dosage, 4.0 mg/l)



EFFECT OF pH ON THE TURBIDITY REMOVAL OF TWO CLAY SUSPENSION (Clay, 50 mg/l; Alkalinity, 1.0 meq/l)



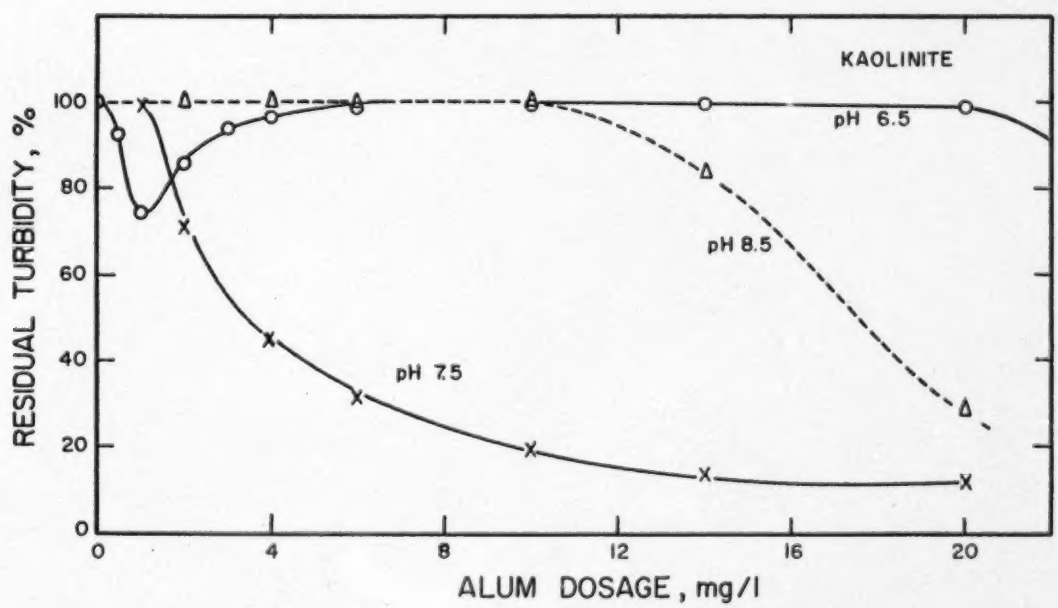
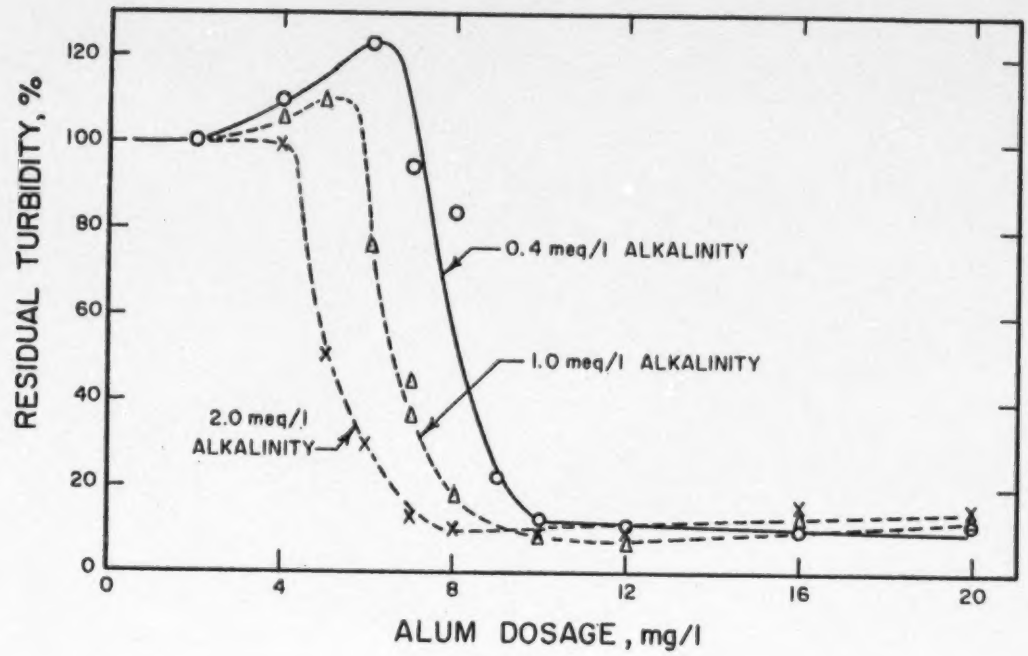


FIGURE 13

EFFECT OF ALKALINITY ON THE TURBIDITY REMOVAL AND MOBILITY OF BENTONITE SUSPENSIONS (At pH 7.5)



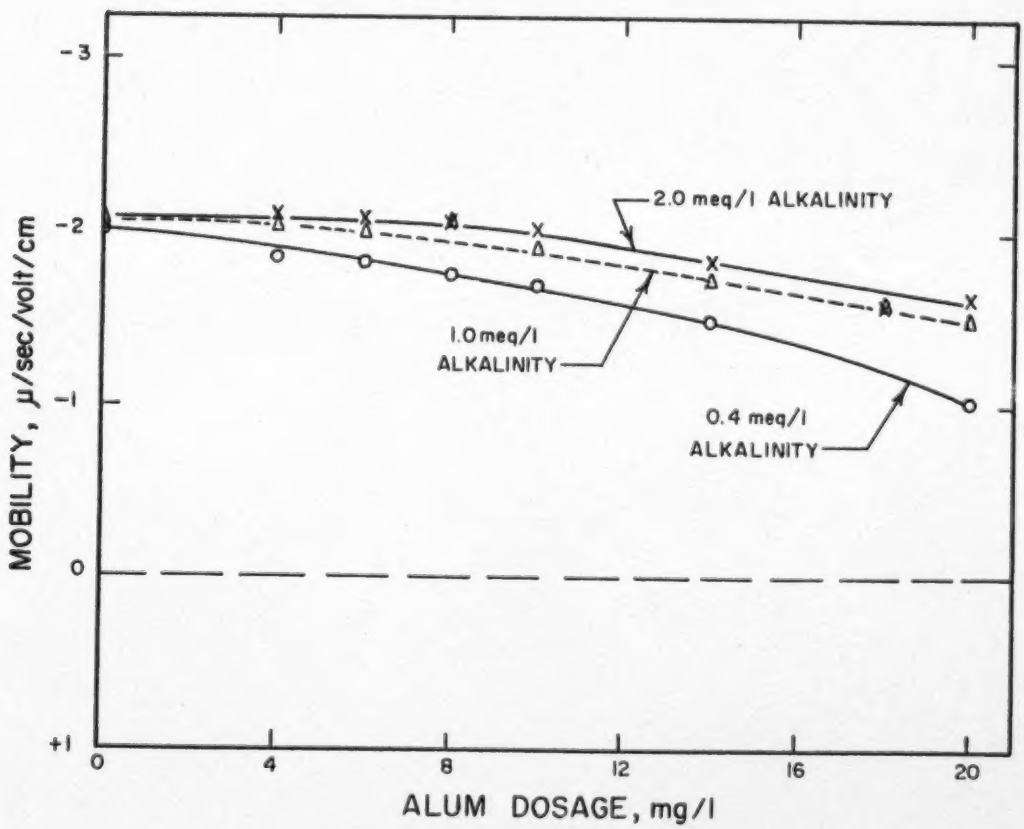


FIGURE 14

EFFECT OF ALKALINITY ON THE TURBIDITY REMOVAL AND MOBILITY OF KAOLINITE SUSPENSIONS (At pH 7.5)

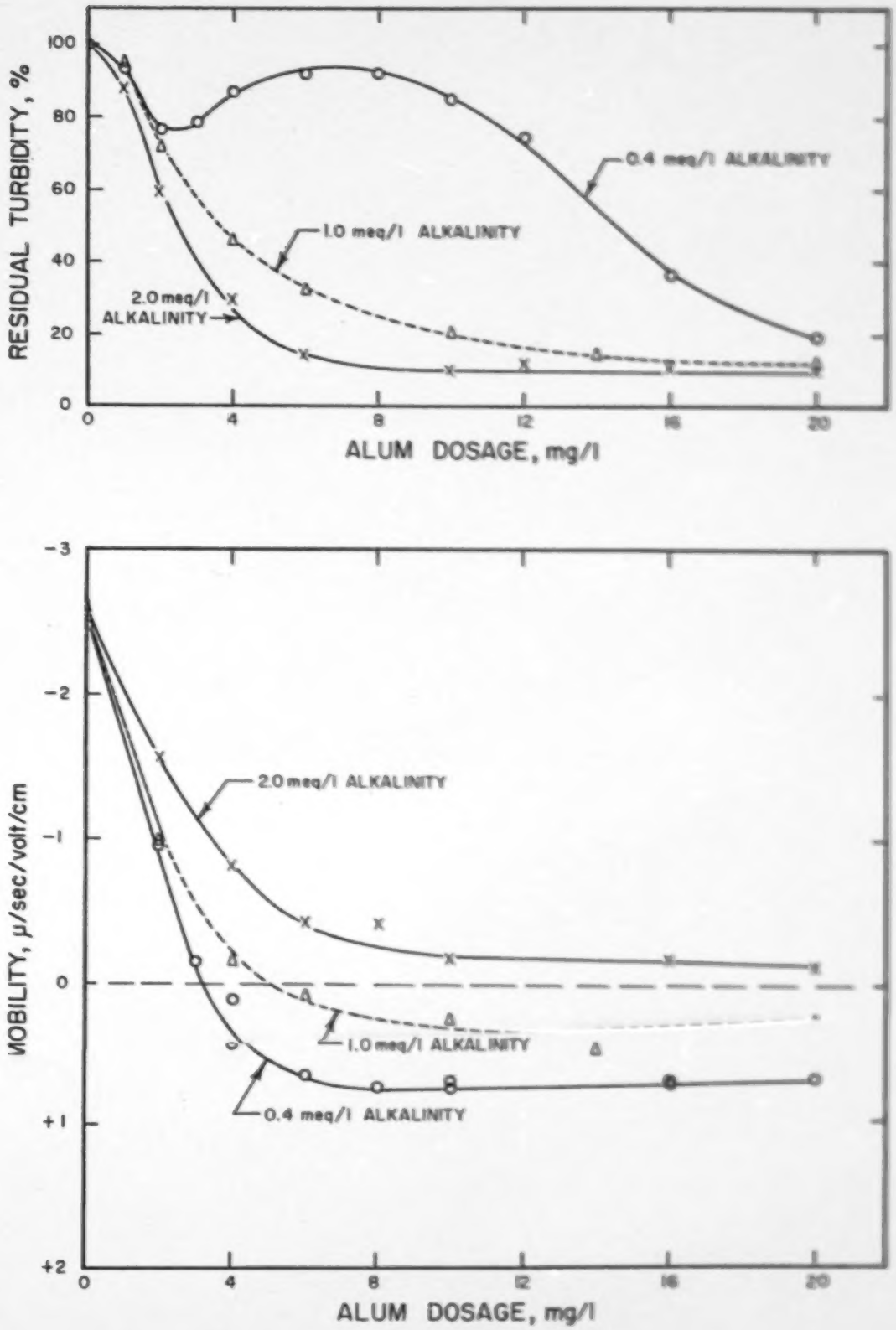


TABLE VI

EXPECTED ELECTRIC CHARGE OF THE HYDROLYSIS PRODUCT OF ALUM FOR THREE ALKALINITIES

Conditions Set			
Initial Alkalinity meq/l	0.4	1.0	2.0
Isolelectric pH (pH_i)	8.0	7.6	7.3
pH maintained	$7.5 < pH_i$	$7.5 < pH_i$	$7.5 > pH_i$
Expected Electric charge of Hydrolysis Product of Alum	Positive	Slightly positive	Slightly negative

The mobility data in Figures 13 and 14 bear out the expected result, i.e, the change of initial negative mobility for both clays was more affected at low alkalinity.

One important difference between the two clay suspensions was the change in mobility. Only a slight decrease in the negative mobility induced rapid coagulation with the bentonite suspension; whereas, a significant mobility reduction was required for good coagulation with the kaolinite suspension. At the same alum dosage, the turbidity removal was more effective at high alkalinity (at pH 7.5).

Effect of Clay Concentration

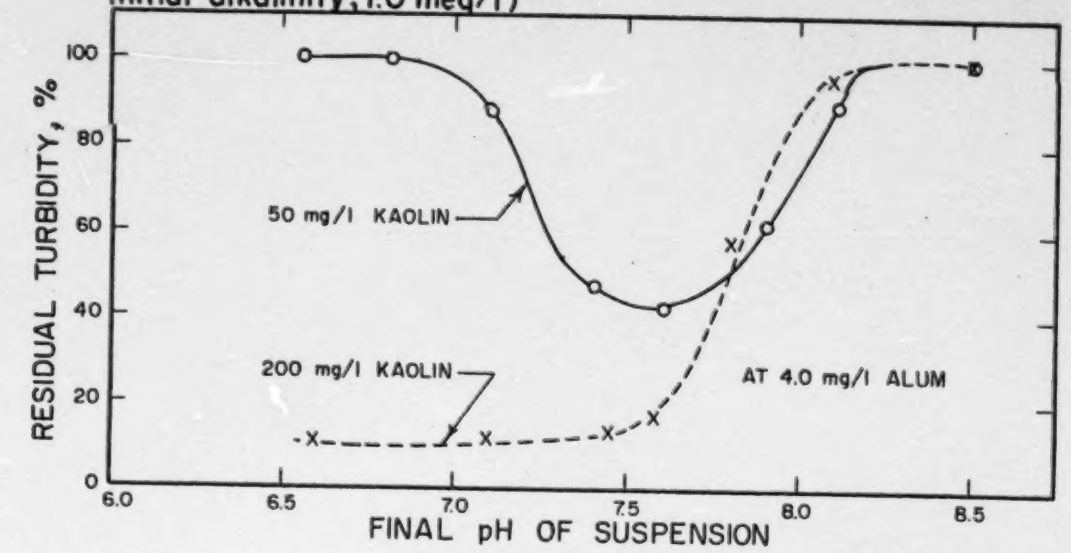
In order to determine the effect of concentration, the clay concentration previously used was increased four times to 200 mg/l.

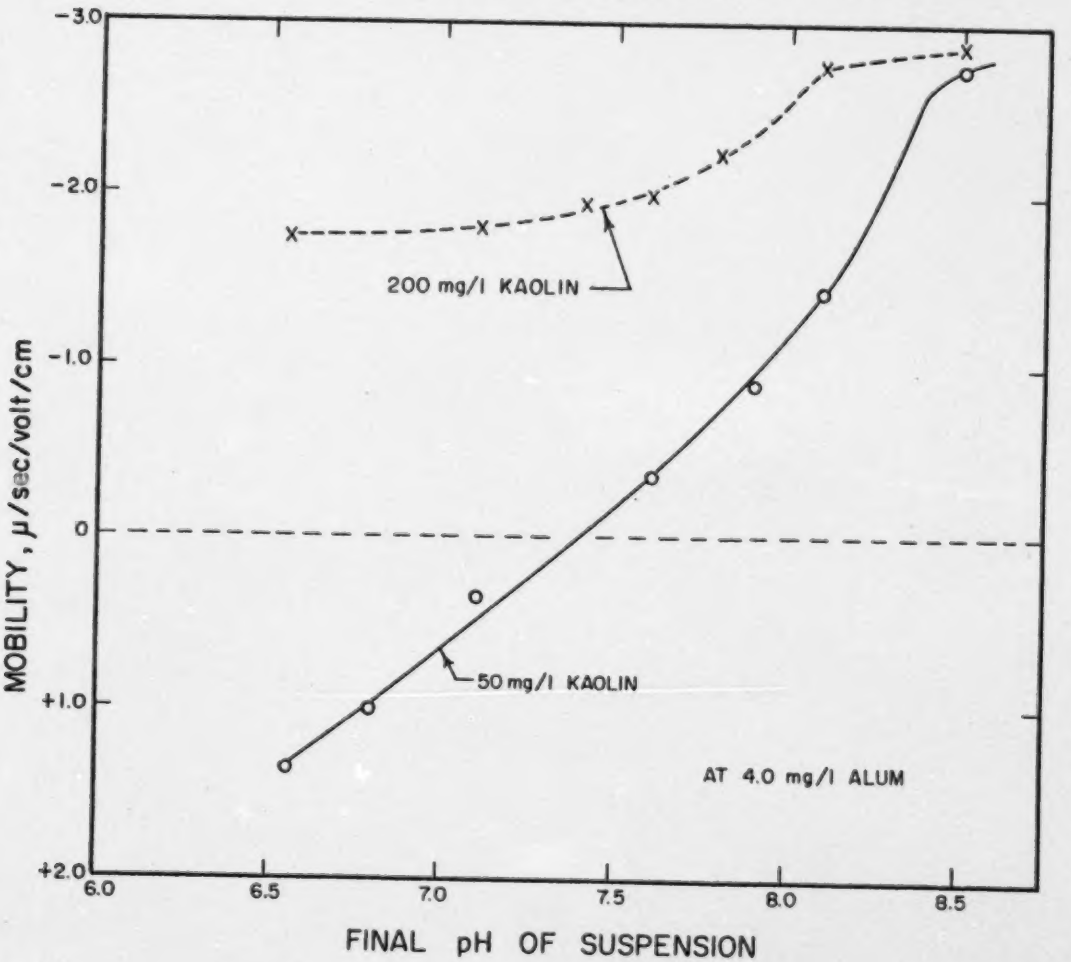
Figure 15 shows the coagulation curve and the mobility curve for a constant alum dosage in kaolinite suspensions. Unlike the low-concentration kaolin suspension (50 mg/l) the 200 mg/l kaolin suspension did not show the dip in the turbidity - pH coagulation curve. It did show that a pH lower than pH_i resulted in a better removal of turbidity. Mobility results also varied greatly with concentration of clay. At high kaolinite concentration, good coagulation took place even though the mobility reduction was relatively small.

Figure 16 shows the coagulation curve for two clays at two clay concentrations for a pH of 7.5. The difference between the two clays was shown by the fact that the increase in bentonite concentration led to an increase in alum dosage required for good flocculation; whereas, the reverse was true for kaolinite suspensions.

FIGURE - 15

EFFECT OF KAOLIN CONCENTRATION ON THE TURBIDITY REMOVAL AND MOBILITY OF CLAY (Alum dosage, 4mg/l; Initial alkalinity, 1.0 meq/l)





EFFECT OF LIME USED IN pH CONTROL

In the foregoing experiments, NaOH and HCl were used to control pH. Since lime is cheaper and a more commonly used alkaline chemical than NaOH, it was decided to check our results with the use of lime in place of NaOH. Results shown in Figure 17 indicated that there was no difference in the turbidity removal depending on whether lime or NaOH was used in pH control.

FIGURE 16

EFFECT OF CONCENTRATION OF TWO CLAYS ON THE TURBIDITY REMOVAL (Alkalinity, 1.0 meq/l; pH=7.5)

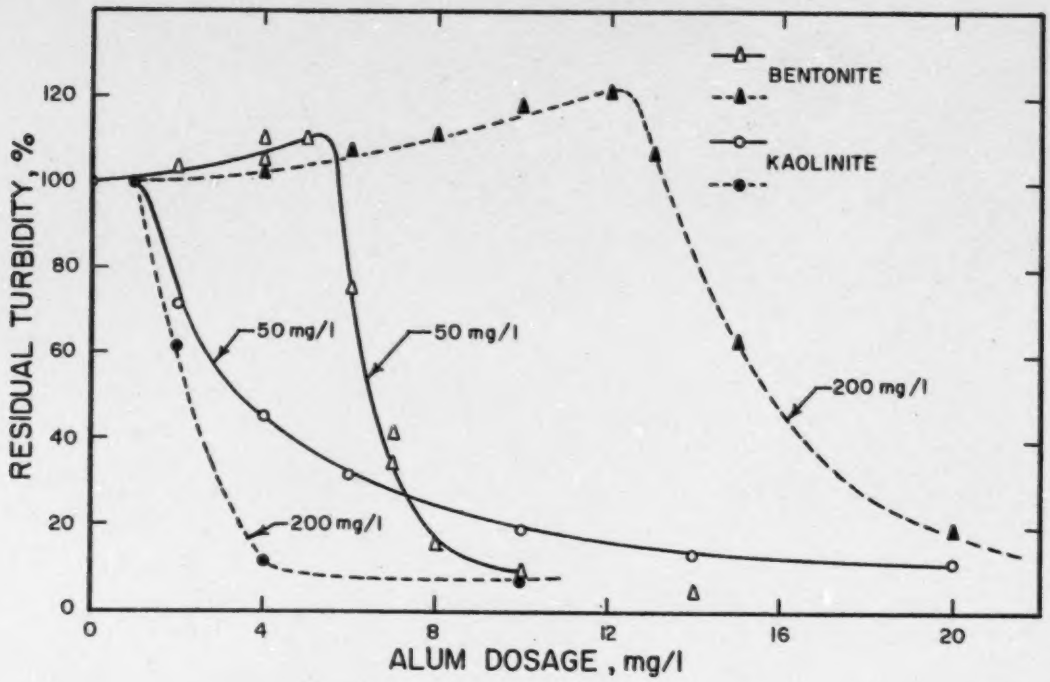
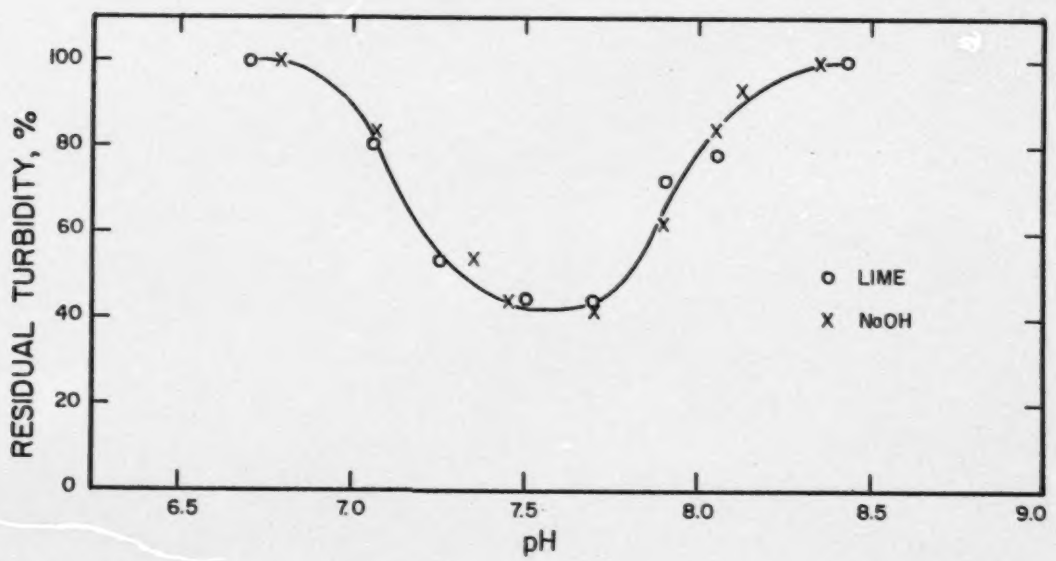


FIGURE 17

EFFECT OF THE KIND OF ALKALINE CHEMICAL USED FOR pH CONTROL (Kaolinite, 50 mg/l; alkalinity, 1.0 meq/l; alum dosage, 4.0 mg/l



VIII. DISCUSSION OF RESULTS OF pH-CONTROLLED COAGULATION

The results of the investigations of pH-controlled coagulation will be discussed and explained in view of presently accepted theories of colloid science in order to aid in the understanding of the mechanism of turbid water coagulation.

RELATIONSHIP BETWEEN THE ISOELECTRIC pH OF $Al(OH)_3$ AND ALKALINITY

Before discussion of the results, it may be necessary again to clarify the terms used. Optimum pH was used in the present studies to mean the pH at which good coagulation took place with the formation of a large fast-settling floc, at a minimum alum dosage. Isoelectric pH was the pH at which the net charge of the aluminum-hydroxo complex was zero and corresponded to least solubility. Optimum pH and isoelectric pH are not synonymous, although they can be the same for certain conditions of suspension.

The results of study on the 50 mg/l kaolinite suspension, shown in Figures 8 and 9, led to the conclusion that the optimum pH for the low-concentration kaolinite suspension was a function of bicarbonate alkalinity, and that at the optimum pH the charge of hydrolyzed alum was neutral.

According to Packam (6), the optimum pH of coagulation corresponds to a pH at which aluminum hydroxide is least soluble; i.e., at the isoelectric pH (pH_i) of the aluminum-hydroxo complex.

Considering that the clay particles acquire the charge of the adsorbed aluminum-hydroxo complex, when the clay surfaces are completely covered, the results of Figures 8 and 9 are consistent with Packam's results.

However, our results indicated that the pH_i (isoelectric pH) was dependent on the bicarbonate concentration whereas Packam showed that pH_i was about 7.0.

The results of Packam (19) and Black (17) were compared with ours from the aspect of bicarbonate concentration; the comparison is shown in Table VII:

TABLE VII

COMPARISON OF OPTIMUM pHs

Investigator:	Packam	Black	Eng-Sci.	Eng-Sci.
Type of Clay	kaolinite	kaolinite	kaolinite	kaolinite
Clay Conc.	50.0 mg/l	65.8 mg/l	50.0 mg/l	50.0 mg/l
Bicarbonate Alkalinity	~ 2.5 meq/l (Final)	1.0 meq/l (Initial)	2.5 meq/l (Final)	1.0 meq/l (Initial)
Optimum pH Found	~ 7.0	7.6-7.8	7.05 *	7.6 *

* From Figure 10

Table VII shows that our results are in good agreement with Packam and Black if the bicarbonate concentration is taken into account.

Marion (23) and Stumm (18) observed that the isoelectric pH of the aluminum-hydroxo complex varied with kind and concentration of anions present in the suspension. When an anion has a stronger coordination tendency with aluminum ion than does hydroxide ion, the isoelectric pH decreases with an increase of anion concentration. Phosphate, sulfate, citrate, and tartrate ions are cited as examples of such anions.

The results shown in Figure 10 indicate that bicarbonate ion is also a strong coordinator with aluminum ion. The presence of sulfate ion, which was added to the suspensions as aluminum sulfate, may have affected the above relationship also. However, the work of Marion (23) showed that the effect of sulfate ion was insignificant at sulfate concentrations less than 2.0 meq/l or 114 mg/l as alum (pH_1 decreased 1.0 unit at an increase of ~36.0 meq/l sulfate ion).

Figure 9 shows the double flocculation curve at pH 6.5 (two zones of flocculation). This phenomenon was explained by Kaufman (21) as involving the Coulombic force due to zeta potential and the effect of sulfate ion. Our mobility data agree with his explanation. However, the flocculation was slight at the pH (pH 6.5) and was much less than at pH_1 (7.6), even though the particle charge was neutralized to zero. The absence of double flocculation at pH 7.5 or pH 8.5 in Figure 9 may have been due to the neutral or negative charge of the hydrolysis product of alum.

OPTIMUM pH vs. ISOELECTRIC pH of $Al(OH)_3$

The results shown in Figures 11, 12, and 15 indicate that the optimum pH of coagulation is not always the same as the isoelectric pH (pH_1) of the alum hydrolysis product. The better coagulation at the smaller alum dosage was attained at a pH lower than the pH_1 when the suspensions was bentonite or a high concentration of kaolinite. Also, for these two suspensions, good coagulation does not occur simultaneously with a great reduction in negative clay charge, as shown by Figures 13 and 15. From these observations and the observations on low-concentration kaolinite suspensions, the following explanation was offered:

According to Kruyt (24), the flocculation of colloidal particles is controlled by the probability of collision and the probability of adhesion. The former depends on the temperature and concentration, and the latter depends mainly on the electrical charge.

The probability of collision increases with the increase in the number of particles per unit volume according to the following:

Smoluchowski's equation for maximum coagulation rate based on the assumption of 100 percent inelastic collision is:

$$-\frac{dN}{dt} = KN^2 \qquad (1)$$

N = number of particles per unit volume
t = time
K = constant

The rate constant K was shown by Whytlaw-Gray (25) to take the form of:

$$K = \frac{2RT}{3\eta} S \times \frac{1}{N}\left[1 + \frac{AxL}{r}\right] \qquad (2)$$

R = gas constant
T = absolute temperature
η = viscosity of the medium
S = ratio of the radius of the sphere of influence around spherical particle to the actual radius of the particle ($\doteq$ 2.0)
A = constant
L = mean free path of the molecules of the medium
r = radius of a particle

Substituting into equation (1):

$$-\frac{dN}{dt} \doteq K'N + \frac{K''N}{r} \qquad (3)$$

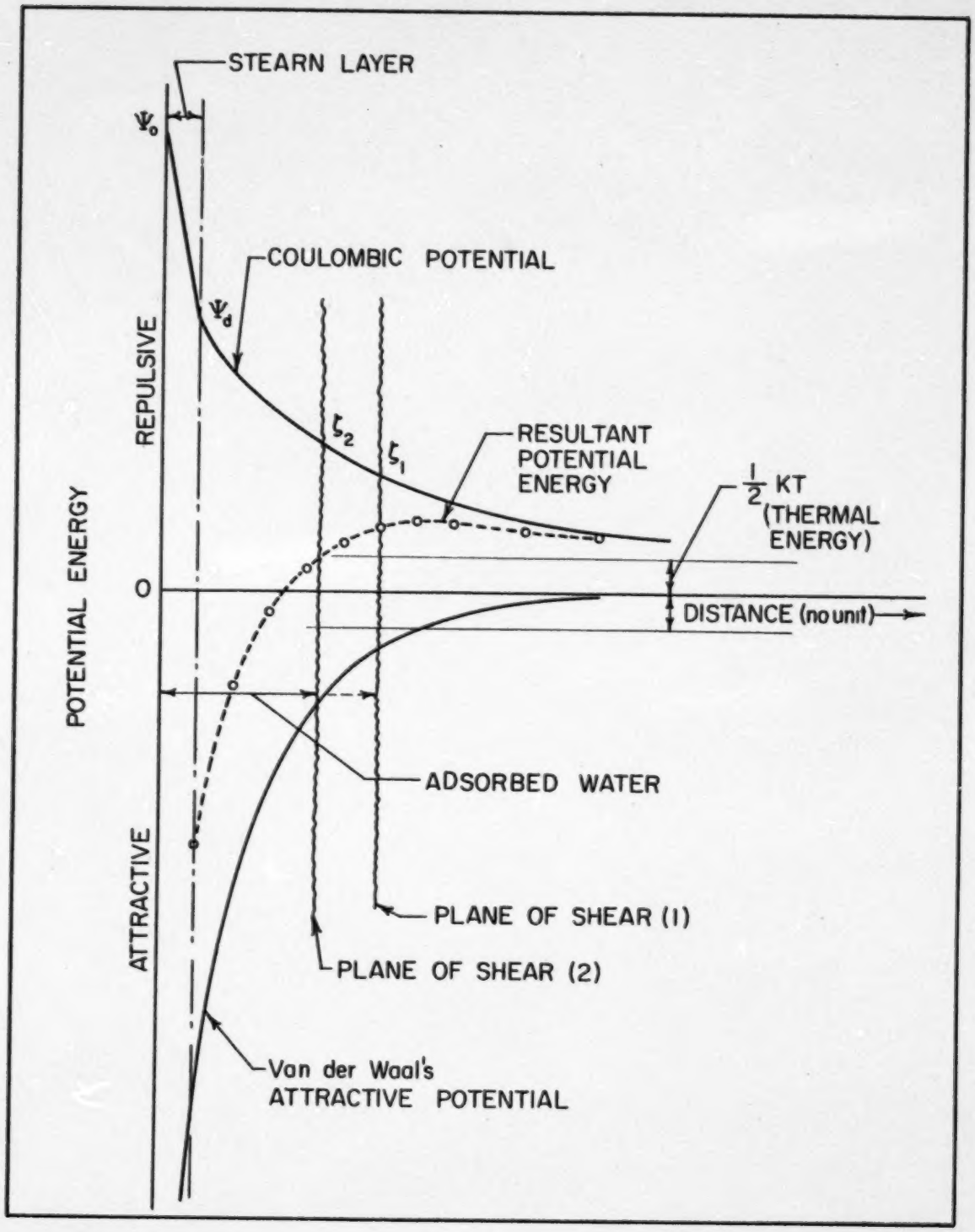
N = number of particles/unit volume
t = time
K, K', K'' = constants
r = radius of a particle

An increase of N can be attained either by an increase of weight concentration, at constant size distribution, or by a decrease in average size, at constant weight and volume fraction. In the first case, the increase in the probability of collision is obvious. In the second case, the increase of N is proportional to $\left[\frac{1}{r}\right]^3$. Therefore, this case will also result in an increase in the probability of collision, according to equation (3).

With a decrease in particle size, the probability of adhesion is expected to increase, which is indicated by the comparison of Coulombic energy distribution around planar and spherical particles. In comparing spherical with planar surfaces, Bier (26) noted "there is relatively more volume available far away from the interface than close to it. Consequently, those parts of the double layer

FIGURE 18

THE STRUCTURE OF THE DOUBLE LAYER AND THE CORRESPONDING POTENTIALS



where the potential is low are relatively more important than the flat double layer . . . ". Hence it is not difficult to deduce that the smaller the particle is the more the surface is curved, and the easier the approach to close distance.

At high particle concentrations, coagulation took place even at relatively high values of negative mobility, as shown in Figures 13 and 15. A reason to be cited on this is the fluctuation of thermal energy. In order to exhibit adhesion, a particle must overcome the resultant repulsive potential barrier as shown in Figure 18. When the one-dimensional thermal energy expressed as $E_k = 1/2$ KT is greater than the maximum of the resultant potential, adhesion takes place. However, the thermal energy of Brownian movement is a statistical average, and the Maxwell-Boltzman distribution law indicates that there is a fluctuation from the average value. Therefore, some particles may overcome the potential barrier even at a significantly high zeta potential (and consequently a high potential barrier of adhesion).

From this reasoning, good coagulation can take place even with only a slight decrease of zeta potential.

The number of particles includes insoluble aluminum-hydroxide as well as clay particles. For a suspension with a small number of particles, good flocculation can be induced by an increase in the number of colloidal particles in the form of $Al(OH)_3$. Therefore, the isoelectric pH led to good coagulation for a low-concentration (50 mg/1) kaolinite suspension. The mere reduction of clay charge did not increase the probability of collision even though the probability of adhesion was enhanced, and only slight coagulation took place, as shown in the curve for pH 6.5 in Figure 9.

If the suspension has a sufficient number of particles per unit volume (which induces a large number of collisions) so that a slight increase in the probability of adhesion can result in rapid coagulation, a slight decrease in zeta potential by alum will result in good flocculation. For this purpose, the cationic hydrolysis product of alum is better than the isoluble and neutral $Al(OH)_3$. Therefore, a pH lower than the pH_i is favorable for coagulation. This was the case with the bentonitic suspension and the high-concentration kaolinite suspension, as shown in Figures 12, 15, and 16.

In this reasoning, it was assumed that the bentonite suspension had a larger number of particles per unit volume than the kaolinite suspension at the same weight concentration. This assumption was based on the following facts:

1. Rolfe (11) noted that the average size of bentonite is less than 0.5μ; whereas, that of kaolinite is about 1.0μ.

2. The turbidity of the 50 mg/1 kaolinite suspension was 60 ppm; whereas, the same concentration of bentonite was 25 ppm on the silica scale.

3. As shown in Figures 11, 12, and 13, the increase in turbidity at the initial stage of coagulation was observed only in the bentonite suspension but not in the kaolinite suspension. In addition, the increase in turbidity was more pronounced when the alum hydrolysis product was charged positively than when it was neutral or negative.

   A similar observation was made by Mackrle (27); he explained that the increase was caused by the formation of colloidal $Al(OH)_3$. However, the absence of turbidity increase in the kaolinite suspension and the more pronounced increase at a pH lower than pH_i (Figure 11), where the alum hydrolysis product was present, for the most part, as soluble and positive ions, was not consistent with his explanation.

   We attempt to explain this phenomenon from the point of view of increase in the size of particles. When the sub-microscopic sizes, which do not scatter visible light, agglomorate to a size large enough to scatter light, the increase of turbidity is observed. The increase in particle size by agglomeration is enhanced by the charge reduction caused by Al^{+++}.

The reversal of slope at low CEC in the CEC-D_{50} alum dosage plot, as shown in Figure 6, may be explained by the preceding discussion. The low CEC, which is due to a low concentration of kaolinite, corresponds to a small number of particles per unit volume. In order to provide a sufficient number of collisions to induce rapid coagulation, more particles in the form of $Al(OH)_3$ must be added. Therefore, more alum was needed in the suspension as the concentration of kaolinite became less. Stumm (18) stated, "Thus, at the isoelectric point, only a fraction of the hydrolysis species present are really isoelectrical; some species are positively or negatively charged." Conversely, at a pH other than pH_i, a certain fraction may be insoluble isoelectric hydrolysis species.

EFFECT OF ALKALINITY ON TURBIDITY REMOVAL

The results shown in Figures 11, 13, and 14 indicate that the effect of alkalinity is important not only on pH_i but also on the degree of clarification. Figure 11 shows that for a given alum dosage, with pH_i corresponding to alkalinity, a better turbidity removal could be achieved at the higher bicarbonate concentration. This result may be explained by one or both of the following reasons:

1. With an increase in bicarbonate alkalinity, more bicarbonate ions are coordinated into the aluminum-hydroxo complex. This can explain above effect if we assume the complex is less soluble than $Al(OH)_3$.

2. With an increase in Na^+, in the form of $NaHCO_3$, the concentration of Na^+ in the fixed part of the double layer also increases.

Colloid scientists, Alexander (28) and Mysel(29), assume that the thickness of the solvated layer of colloids (which is the boundary of the zeta potential) is a monomolecular thickness of water. However, soil scientists hold different opinions regarding clay particles. Grim and Cuthbert (30) concluded that the non-liquid film (which is held tightly to clay) has a thickness of three molecular layers of water (~7.5 Å) for Na^+ - montmorillonite; whereas, the thickness is four molecular layers or about 10 Å, for Ca^{++} - montmorillonite. This decrease in solvated layer thickness by an increase of Na^+ in the layer led to the increase of zeta potential, as shown in Figure 18 ($\zeta_1 \longrightarrow \zeta_2$). But, the increase of van der Waals potential accompanied the decrease of thickness also. The increase of van der Waals potential may be greater than that of the zeta potential, the former being a short-range force. Therefore, the resulting potential is more favorable for adhesion of particles and coagulation.

IX. SUMMARY AND RECOMMENDATIONS

SUMMARY AND SIGNIFICANCE OF THE RESULTS

Kaolinitic suspensions are generally difficult to coagulate by mere addition of alum. Through the control of pH, optimum coagulation conditions can be achieved in which an increase in floc size and decrease in alum dosage result.

For low-concentration kaolinitic suspensions (<50 mg/l), the pH to be attained is the isoelectric pH (pH_i) of the aluminum-hydroxo complex. This pH_i was found to be dependent on the suspension alkalinity. The relationship between pH_i and bicarbonate alkalinity was established. With bentonitic suspensions and with high-concentration kaolinitic suspensions, the optimum pH was less than the pH_i value for the suspension. These observations were explained.

A method of metermining the type of clay in a suspension was proposed. A turbidity/CEC ratio can be used to determine approximately whether the clay suspension is bentonitic or kaolinitic.

A method for measuring cation exchange capacity (CEC) of dilute clay suspensions was developed. The use of methylene blue dye made the procedure simple and the results reporducible.

In the case of bentonitic suspensions, the measurement of CEC and alkalinity may be used to predict alum dosage for coagulation for a particular plant condition.

As yet, there is no sufficient basis for determining which chemical treatment should be used and which coagulant aid (such as bentonite) and how much alkalinity should be added to a given suspension to produce the best flocculation at minimum cost. It is hoped that the results in the present tests will shed light in this area, providing a pH-controlled coagulation depending on the suspension alkalinity and the type of clay.

Other important variables to be considered in the search for optimum coagulation conditions are the use of bentonite and the addition of alkalinity.

RECOMMENDATIONS FOR FURTHER STUDY

In view of our laboratory results, it appears to be desirable to control pH for improved coagulation. The effect of coagulation aids in the form of bentonite or alkalinity was found to be very important.

The advantages and practicality of this approach should be tested in plant operations. Jar tests usually show qualitative results, and these results sometimes

deviate from actual results of plant operation due to hydraulic dissimilarity and other physical factors. However, field operations are limited in the range of control of such variable factors as the type of clay, alkalinity, pH, mixing time and speed, settling time, etc. A pilot plant study will allow the simulation of plant conditions to a certain degree by providing for continuous treatment. Prediction of performance and imporvement may be made possible.

In order to evaluate the overall water treatment process, for each different clay, pH, and other different conditions of treatment, models of a coagulation basin, a settling basin, and a filtration column should be built.

For improvement in the settling facilities, the use of shallow-depth, multi-storied settling basins is proposed. It is acknowledged that the efficiency of a settling basin increases with a decrease in depth if the same detention time is used. So far, the difficulty of sludge removal and the difficulty in the construction of multi-storied basins have hindered the use of this type of basin. The advantages of the multi-storied basin can be significant in reducing short-circuiting, reducing detention time and/or increasing effluent clarity, and reducing light penetration which leads to less algal growth. In Sweden (31) this type of basin is being used. Considering the present trend toward better pre-treatment and higher filtration rates, for increasing treated water production, this type of basin should be evaluated more seriously.

An aspect worth considering in the construction of a multi-storied settling basin is the direction of scraper movement for removing sludge. Maynard (32) noted that the moving of the scraper in the direction of hydraulic flow may be advantageous in the reduction of eddies and disturbance, which can be significant when the scraper is moved counter-currently. The present use is commonly counter-current collection of sludge; this practice can be improved.

The ratio of mixing time to settling time should also be investigated with respect to the best settled effluent. If good chemical coagulation and flocculation by mixing are achieved, the floc settles very rapidly (within 30 min for 16 ft depth). Therefore, an increase in mixing time and a reduction in settling time, when the mixing and settling are confined in the same basin, may increase turbidity removal. With better coagulation and settling, the turbidity of a filter influent can be reduced to less than 1.0 ppm, and the filtration rate can be increased as much as possible to the limit at which alum floc breaks through. To this end, anthracite filter media, upflow-type filtration, and poly-cations and anions (as filter aids) should be investigated.

All the foregoing improvements should be evaluated in terms of turbidity removal and filterability. For the turbidity measurement, it was found that a fluorometer, used as a nephelometric deivce, can detect turbidity as low as 0.02 ppm with a few milliliters of sample. For the measurement of filterability, the silting index apparatus developed by the Millipore Filter Co. can be used for simple and fast operation. The silting index data can be compared with actual filtration rates using a filter column of sand.

It is customary to adjust pH after filtration for the purpose of scale control. pH is also important in post-chlorination. For the coagulation process, the optimum pH depends on the suspension alkalinity and the type of clay; it ranges approximately from pH 6.0 to 8.0. For scale control, the optimum pH varies widely, but is is generally greater than pH 7.0. For chlorination, a low pH (less than 6.0) is better for the colicidal effect. Hence, the manner of pH control in the water treatment process will affect the economy of chemical application. This factor needs systematic investigation.

Color in raw water is mostly associated with waters of low concentrations of suspended matter; turbid water is not highly colored. This is usually explained as being due to the adsoprtion of coloring material on the suspended particles. If this is true, a colored water may be treated by adding highly adsorbing clay and by coagulating with alum at an ordinary pH of approximately 6.0 to 8.0. Black (33) noted that organic color can best be removed by ferric sulfate at a low pH of approximately 3.0 to 4.0. The use of bentonite and alum coagulation in color removal may be advantageous compared to the ferric sulfate treatment at low pH from the point of view of chemical cost for adjusting pH. The quantitative evaluation of the color removal method utilizing bentonite and alum warrants investigation.

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